

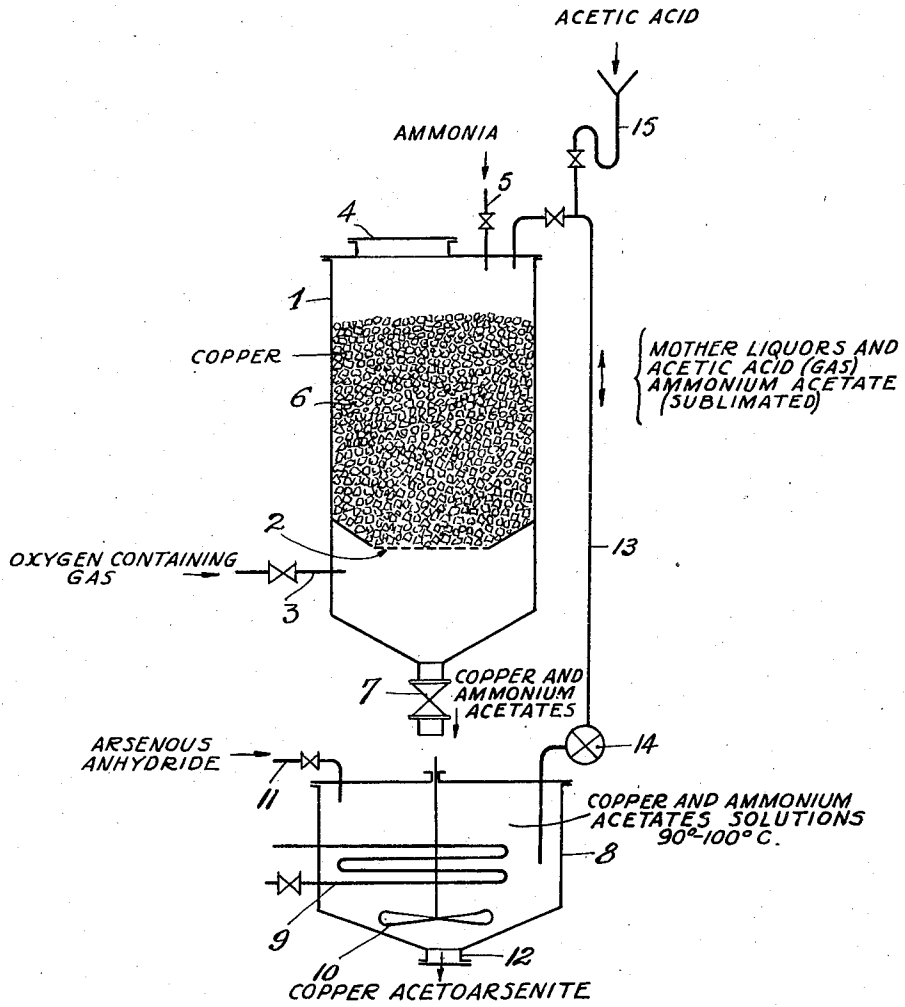
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MANUFACTURE OF COPPER ACETOARSENITE OR SCHWEINFURT GREEN

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MANUFACTURE OF COPPER ACETOARSENITE OR SCHWEINFURT GREEN

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8 Claims. (Cl. 260—438)

The invention relates to the manufacture of copper acetoarsenite $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{Cu}(\text{AsO}_2)_2$.

It is known that to obtain a product showing a nice colour, the manufacture of the aforesaid compound is more or less difficult owing to the influence of factors such as the impurities, the quality of the materials used and the working conditions (temperature, duration of the operation, concentration of the reagents, stirring and so on).

The manufacture of the product from copper arsenite and copper acetate is not satisfactory as instead of the beautiful bright green desired a light greyish green precipitate is obtained.

On the other hand said compound is not easily obtained by the reaction of the arsenous anhydride on the copper acetate through prolonged boiling, and this process is not of commercial application.

Thus, until now, processes have been applied using very pure materials according to which the arsenous anhydride is dissolved in a heated state with sodium carbonate, and then submitted to the action of a boiling solution of copper sulfate in order to form the copper arsenite. To this copper arsenite is added acetic acid at 6° Bé., after which the solution is agitated and the precipitate allowed to settle. The precipitate then changes progressively from the dirty green to a bright green colour. The resulting mother liquors are treated separately by means of lime or sodium hydroxyde to obtain greens of inferior grades.

In this process aside from the numerous steps, a part of the reagents is lost and the yield is low, being of the order of 67-68% of the theoretical yield.

The invention has for its object a process for manufacturing copper acetoarsenite which is simple and gives a nice coloured product with a yield approaching the theoretical yield.

It has been found that if, on copper acetate and in the presence of ammonium acetate, and for instance on a solution of copper and ammonium acetates (cupro-ammonium acetate), there is caused to act arsenous anhydride or a salt, particularly an alkaline salt, of the arsenious acid, while raising the temperature to 90-100° C., copper acetoarsenite rapidly forms which possess a beautiful bright green colour.

Accordingly the invention consists in causing to act on copper acetate, in the presence of ammonium acetate, and for instance on a solution of copper and ammonium acetates, a reagent formed of arsenous anhydride, or a salt, particu-

larly an alkaline salt, of the arsenious acid, and heating the mixture to temperatures of between 90-100° C. in order to obtain copper acetoarsenite which is separated.

The copper acetate as well as the ammonium acetate used may be obtained from any suitable source, and the solutions such, for instance, as the solution of the copper and ammonium acetates may be prepared in any suitable or convenient manner but, preferably, use is made of a copper acetate, or a solution of copper and ammonium acetates obtained from the attack of copper, or a copper bearing material, by means of a liquor containing acetic acid or a derivative and ammonia or a derivative, which liquor is caused to act on the copper or copper bearing material in the presence of an oxygen containing gas, which may be more or less pure oxygen or preferably a current of air.

Therefore the invention also consists in using as a copper acetate or as a solution containing copper and ammonium acetates, the copper acetate or a solution of copper and ammonium acetates obtained in attacking, in the presence of an oxygen containing gas, copper or a copper bearing material, by means of a liquor containing acetic acid or a derivative and ammonia or a derivative.

It has further been found that the ammonium acetate appears to enhance considerably the dissolution of the arsenous anhydride and to increase the solubility of the copper acetate, forming a more soluble double salt of copper and ammonia.

Therefore and in accordance with the invention solutions of copper acetate and ammonium acetate or of copper and ammonium acetates of high concentrations may be used, resulting in yields of high values, almost theoretical in copper acetoarsenite.

The presence of ammonium acetate not only enables high concentrations to be used but also to conduct the operation in the presence of undissolved copper acetate, which passes gradually and easily into solution as the copper acetoarsenite forms.

The process is thus further characterised by the fact that the operation may be conducted in the presence of an excess or reservation of undissolved copper acetate, which passes progressively into solution as the copper acetoarsenite forms.

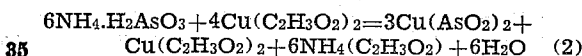
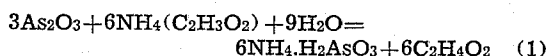
Further, it has been found that the ammonium acetate used in the process is continuously regenerated during the operation while acetic acid

forms which may be used to obtain further quantities of copper acetate.

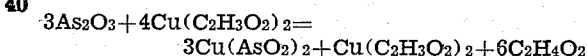
As a result the process may be carried out in a cyclic manner, the ammonium acetate being continuously placed in the presence of the copper acetate already formed, or introduced, eventually together with acetic acid, in the liquor used for attacking a copper bearing material. The acetic acid of the copper acetate formed or of the liquor may be, at least by part, acetic acid from the forming reactions of the copper acetoarsenite.

Thus the invention also consists in a cyclic process of forming copper acetoarsenite by means of ammonium acetate, in which the ammonium acetate is regenerated and free acetic acid is formed in the course of the formation of the copper acetoarsenite, and in which the ammonium acetate is caused to meet copper acetate already formed or the said ammonium acetate is introduced, eventually together with acetic acid, in a reaction liquor for attacking a copper bearing material used to form copper acetate, while the acetic acid formed is used either for any desired purpose or, preferably, to form the said copper acetate.

From the searches and experiments of the applicant, it seems to result that the copper acetoarsenite forms in accordance with the following reactions:



It should be observed that it looks as if the copper acetoarsenite directly forms from the arsenous anhydride and the copper acetate while acetic acid is liberated, as follows:



It results that the quantities of materials used are those necessary for forming the copper acetoarsenite.

By way of example, the process may be carried out in the following or a similar manner, reference being had to the annexed drawing showing diagrammatically a suitable apparatus.

In a tower 1 which is provided with a false perforated bottom 2, with a pipe 3 for introducing under the false bottom a current of an oxygen containing gas, for example air, obtainable from any suitable source not shown, and with an inlet 4 and a pipe 5 for the supply of the other reagents, copper or a copper bearing material 6 is arranged on the false bottom 2, while a reaction liquor is supplied through 5 and air or another oxygen containing gas is supplied through the pipe 3.

The reaction liquor may contain, for example, 150 to 200 grams of ammonium acetate per liter.

Concentrated solutions of copper and ammonium acetates are collected at the outlet 7 and transferred to any suitable vessel 8 provided with any suitable heating appliance such as the heating coil 9, and preferably also with an agitator 10.

In this vessel is introduced through 11 arsenous anhydride from any suitable source (not shown), and the mixture is then heated to 90–100° C. by means of the coil 9, the solution being concentrated as far as possible to be sure that no copper acetoarsenite remains therein.

The copper acetoarsenite is separated and re-

moved through the outlet 12 and thereafter washed and drained; the mother liquors, to which acetic acid is supplied at 15 in a quantity corresponding to that which has been combined in the copper acetoarsenite, are returned, through, for example, the pipe 13 and pump 14 to the tower 1 to form further quantities of copper acetate.

The acetic acid liberated or evoked, and the ammonium acetate sublimated during the heating to 90–100° C. of the vessel 8 are continuously returned to the tower 1.

The following examples illustrate the invention.

Example 1.—50 to 100 grams of ammonium acetate and 50 grams of copper acetate are introduced in a suitable vessel together with 150 to 200 grams of water. This mixture is heated to 80 to 90° C.

When at least a part of the two salts is dissolved, 55 grams of arsenous anhydride are added in the form of a fine powder, while the heating is continued and the mixture is stirred. Copper acetoarsenite of a beautiful green colour forms progressively which settles on the bottom of the vessel.

After three to four hours about 58 grams of copper acetoarsenite are obtained, which correspond to an useful yield of 97–98%.

Example 2.—A highly concentrated solution of ammonium acetate (20%) is introduced in a reaction tower such as 1 to form solutions of copper and ammonium acetates.

Then, when operating as in the Example 1, that is to say using equivalent quantities of arsenous anhydride, equivalent quantities of copper acetoarsenite are obtained.

Example 3.—The operation is conducted in the same manner as in either of the Examples 1 or 2 as far as the solutions of copper and ammonium acetates are concerned, but the arsenous anhydride is introduced in the form of an alkali metal arsenite. Copper acetoarsenite of a beautiful green colour is again obtained, but the yield is somewhat lower than in the Examples 1 and 2.

Throughout the description and in the appended claims, reference is made to both copper acetate and ammonium acetate. Whenever these two salts are present there is formed, at least to a partial extent, the complex salt, cupro-ammonium acetate. Therefore, it is to be understood that the expression "copper acetate and ammonium acetate" should be interpreted to include cupro-ammonium acetate as well.

It should be understood that the invention is not limited to the details of the process particularly described, but includes the alternatives and the modifications.

I claim:

1. A process of manufacturing copper acetoarsenite, which consists in causing arsenous anhydride to act on copper acetate in the presence of ammonium acetate.

2. A process of manufacturing copper acetoarsenite, which consists in causing arsenous anhydride to act on copper acetate in the presence of ammonium acetate and heating the mixture to 90–100° C.

3. A process of manufacturing copper acetoarsenite, which consists in forming a solution of copper and ammonium acetates and causing arsenous anhydride to act on this solution.

4. A process of manufacturing copper acetoarsenite, which consists in mixing copper acetate and ammonium acetate, dissolving a part of these

salts and causing arsenous anhydride to act on the mixture.

5 5. A process of manufacturing copper acetoarsenite, which comprises forming concentrated solutions containing copper acetate and ammonium acetate and causing arsenous anhydride to act on these solutions.

10 6. A process of manufacturing copper acetoarsenite, which consists in causing arsenous anhydride to act on copper acetate in the presence of ammonium acetate, a part of the copper acetate being in solid form.

7. A process of manufacturing copper acetoar-

senite which consists in causing arsenous anhydride to act on copper acetate in the presence of ammonium acetate, the arsenous anhydride being used in the proportion of 35 grams for 50 to 100 grams of ammonium acetate and 50 grams of copper acetate. 5

8. A process of manufacturing copper acetoarsenite which consists in reacting copper with acetic acid and ammonia in the presence of an oxygen containing gas and treating the reaction 10 product with arsenous anhydride to form copper acetoarsenite.

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