

UNITED STATES PATENT OFFICE.

Fritz Quade, of Berlin, Germany, Assignor to Johann Abraham von Wülfing, of Berlin, Germany.

METHOD OF PRODUCING COMPOUNDS OF FORMALDEHYDE WITH SUGARS.

1,062,501.

Specification of Letters Patent.

Patented May 20, 1913.

No Drawing.

Application filed September 16, 1912. Serial No. 720,650.

To all whom it may concern:

Be it known that I, Fritz Quade, doctor of chemistry, citizen of the Empire of Germany, and residing at Berlin, in the Empire of Germany, have invented a new and useful Method of Producing Compounds of Formaldehyde with Sugars, of which the following is a specification.

My invention consists in processes of producing compounds containing one molecule of carbohydrate (milk sugar, cane sugar, maltose) and one to five molecules of formaldehyde under pressure.

I will now proceed to describe my invention:

It is already known to produce such compounds by evaporating *in vacuo* the sugar with an aqueous formaldehyde solution. But in the preparation of these compounds it has hitherto always been necessary to use more of the aqueous formaldehyde solution than theoretically required. It has now been discovered that this necessity for excess of formaldehyde can be avoided if the respective bodies are mixed in the proportions necessary for the reaction in view, provided that the loss of formaldehyde by heating be prevented. This result is obtained by causing the reaction to take place under pressure. In addition to the saving of formaldehyde, there is a further advantage in being able to raise the temperature up to 110° centigrade inasmuch as use can be made of the fact that it is not necessary to add the milk sugar which is difficultly soluble at lower temperatures to the reaction mixture after it has been brought into solution. It is only necessary in such case to add the 40% formaldehyde solution of commerce to the carbohydrate in its natural condition. By operating in this manner under pressure, the syrups which are obtained when such a carbohydrate is mixed with 40% formaldehyde solution in previously calculated molecular proportion and heated under pressure can be brought to dryness with the lower molecular compounds without perceptible loss of formaldehyde, because there are only small quantities of water to be evaporated; moreover these lower molecular compounds dissociate only feebly and they also give up the water more quickly. On the other hand the removal of the larger quantities of water was coupled in the case of the compounds richer in formaldehyde, with loss of formaldehyde,

which although smaller than when the reactions take place under atmospheric pressure merely, nevertheless disturb the molecular proportions.

I desire to point out, that it has been proposed (see British Patent No. 6653 of 1897) to make a combination of 1 molecule of a sugar of the cane sugar group with 1 molecule of formaldehyde. No reference whatever to the use of pressure occurs in this specification; the excess of water is expelled at below 50° centigrade. By this process "the syrup cannot be evaporated to complete dryness and can only be brought into the dry state by mixing with a sufficient quantity of powdered sugar preferably milk sugar, the particles of the powder so obtained however conglomerate easily together. On exposing this new compound to a temperature of 50 to 60° centigrade, it decomposes back into formaldehyde and sugar, and in the presence of moist air it develops formaldehyde." To render this process workable the patentee proposes to combine the formaldehyde-sugar compound with a haloid alkali, potassic bitartrate, or mixtures thereof. Further, in British Patent No. 25138 of 1909 other methods of producing compounds of malt extract and formaldehyde are set forth and claimed, but there is no reference in this patent also to the use of pressure for retaining the formaldehyde, which forms the distinctive characteristic of the present application.

It has been previously proposed to mingle indifferent materials with the reagents for the purpose of facilitating the drying. It is possible to make use of this already known method by adding indifferent material (such as powdered talc) to my compounds containing no excess of formaldehyde for the purpose of absorbing the water introduced in the form of aqueous formaldehyde solution.

The evaporation of large quantities of water is avoided by my invention when paraformaldehyde of commerce mixed in predetermined proportion with the dry carbohydrates is brought directly into reaction therewith by heating in vessels under pressure to a temperature above 105° centigrade. Such heating produces tough syrups which would present some difficulty in treatment; but the treatment is facilitated if there has been added at the commencement of the reaction an indifferent diluting material

(powdered talc) which diluting material does not affect the reaction but causes the production of solid products which can be easily pulverized. If it be desired to obtain the products richer in formaldehyde free from such additions, then the required compounds can be produced by aid of mixtures of paraformaldehyde with aqueous solution of formaldehyde. (See Example 4.) By aid of this method it is possible to reduce the added quantity of water so much, that its removal can take place without any material removal of formaldehyde.

As pressure vessels autoclaves are used which can be brought in the saline bath to a temperature of 110° cent. The pressure rises to a maximum of 2 atmospheres. The exact determination of the pressure is not important, providing no formaldehyde escapes.

Example 1: 100 parts of cane sugar are heated under pressure with 22 parts of a 40% formaldehyde solution for one hour in the water bath, and the small quantity of water is then evaporated *in vacuo* or in the air at 70° cent., producing the compound 1:1.

Example 2: 100 parts of milk sugar are heated under pressure with 44 parts of 40% formaldehyde solution in a saline bath up to 105° cent. The compound formed is fixed with 300 parts talc, and is dried at 70° cent. in the open air. The mixture contains the compound 1:2.

Example 3: 100 parts of cane sugar of commerce are heated with 56 parts of 40% formaldehyde solution under pressure for several hours in a saline bath to 105° cent. The clear syrup formed is mixed with 400 parts by weight of milk sugar and is freed from water at 70° cent. on flat plates. From the mixture the compound 1:3 can be extracted with alcohol.

Example 4: 100 parts of maltose are mixed under pressure with a mixture of 21 parts of 40% formaldehyde solution and 27 parts of paraformaldehyde of commerce, and heated for several hours in the saline bath

up to 110° cent. The compound is then dried at 70° cent. and gives the molecular proportion 1:4.

Example 5: 100 parts of milk sugar are mixed with 250 parts of talc and 44 parts paraformaldehyde of commerce and the mixture is heated under pressure for several hours to temperatures of from 105 to 110° cent. The compound 1:5 is extracted from it with alcohol.

It is understood that a formaldehyde-forming body may be paraformaldehyde alone or a mixture of formaldehyde and various polymerization products which are usually present in formaldehyde solutions.

I claim:

1. The process of producing a compound containing one molecule of biose and one to five molecules of formaldehyde which process consists in heating the molecular admixtures of a formaldehyde forming body and biose under pressure substantially above atmospheric at temperatures up to 110° cent.

2. The process of producing a compound containing one molecule of biose and one to five molecules of formaldehyde which process consists in heating the molecular admixtures of biose and concentrated aqueous solution of a formaldehyde-forming body under pressure substantially above atmospheric to prevent escape of formaldehyde, and removing the water by evaporation.

3. The process of producing a compound containing one molecule of biose and one to five molecules of formaldehyde which process consists in heating the molecular admixtures of biose and paraformaldehyde exclusively under pressure substantially above atmospheric, whereby indifferent diluting materials such as talc are added to the mass before the commencement of the reaction.

FRITZ QUADE.

Witnesses:

EBERHARD THIELEMANN,
WALGEMAR ROGGE.