

UNITED STATES PATENT OFFICE.

HAROLD HIBBERT, OF WILMINGTON, DELAWARE, ASSIGNOR TO E. I. DU PONT DE NEMOURS POWDER COMPANY, OF WILMINGTON, DELAWARE, A CORPORATION OF NEW JERSEY.

EXPLOSIVE AND METHOD OF PRODUCING THE SAME AND ITS INGREDIENTS.

1,008,333.

Specification of Letters Patent.

Patented Nov. 14, 1911.

No Drawing.

Application filed January 31, 1911. Serial No. 605,801.

To all whom it may concern:

Be it known that I, HAROLD HIBBERT, a subject of the King of Great Britain, residing at Wilmington, county of Newcastle, and State of Delaware, have invented a new and useful Improvement in Explosives and Methods of Producing the Same and Its Ingredients, of which the following is a full, clear, and exact description.

When glycerin is treated with the mixed acids, nitric acid and sulfuric acid, for the production of glycerin trinitrate, glycerin trinitrate is produced, the formula of which is:

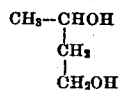


This glycerin trinitrate has certain defects, among which it may be stated that the glycerin which is its base is expensive, and the temperature of explosion of the explosive mixture of the glycerin trinitrate is very high, which makes it in many cases not a good ingredient for smokeless powder.

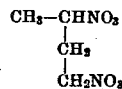
I have discovered that if nitrated butylene glycol be formed, a product is obtained whose temperature of explosive ignition is lower than that of glycerin trinitrate, which enables it to be freely used as an ingredient of smokeless powder, safety explosives and dynamite. Further, I have discovered that such compound may be combined with nitrate derivatives, such, for instance, as nitrated cellulose or nitrated starch, to form a colloid of such mixture. It also may be mixed with glycerin trinitrate, and the resulting mixture has a lower freezing point and is more stable than glycerin trinitrate.

While butylene glycol is known and is described in text books, I believe myself to be the first to have discovered nitrated butylene glycol and its value for the purposes named. Further, the method of making butylene glycol, as set out in the text books, is so complicated as to render it very expensive and difficult to carry out. My discovery, therefore, includes a simple method for directly producing this butylene glycol as well as the nitrated butylene glycol.

The butylene glycol is represented in formula in the following manner:



and when nitrated the formula is thus represented:



I produce the butylene glycol in the following manner, whereby a highly concentrated solution of butylene glycol is directly obtained in one operation from acetaldehyde, and the cost of evaporation, etc., is thereby very much diminished: I take ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$), which may be de-natured without affecting the result. This ethyl alcohol is first oxidized. Preferably I accomplish this oxidation by the ordinary catalytic oxidation, such for instance, by using metallic platinum, copper or zinc and heat. The resultant is acetaldehyde ($\text{C}_2\text{H}_4\text{O}$). This acetaldehyde is then condensed. I have used for this condensation an aqueous solution of an alkaline carbonate, for instance, potassium carbonate; 450 grams of acetaldehyde were cooled to a low temperature say $+5^\circ$ to -10° C. preferably -5° C. and 200 grams or thereabout of powdered ice then added. A few drops of a cooled solution of potassium carbonate containing for example 19 grams of the carbonate in 80 cubic centimeters of water were introduced into this mixture, the temperature not being allowed to rise above 10° C. and preferably not above 5° C. After standing some 10 or 15 minutes a further quantity of the carbonate solution was introduced to the mixture kept at a low temperature and again allowed to stand, contents, being kept as nearly as possible at a temperature of about 0°C .

After the whole of the carbonate had been added, the reaction-product was kept in ice-water for several hours to prevent any rise of temperature and then for a further 20 hours at say $+10^\circ$ C. and at least below 15°

C. If the pure acetaldol is required this may be extracted with ether, but for the purpose of obtaining butylene glycol this is unnecessary. The condensation can be produced
5 by other alkaline carbonate or a borate, phosphate, acetate or cyanid, of the metals of the alkalies or of the alkaline earths, and where, in the claims, I mention an alkaline salt, I mean to include as equivalents
10 salts of metals of the alkalies or of the alkaline earths. The resultant of this condensation is acetaldol ($C_4H_8O_2$). This condensation product is then directly reduced to butylene glycol by means of a reducing agent, and
15 I have employed the following method: The aqueous solution of acetaldol, obtained by condensing 450 grams of acetaldehyde with potassium carbonate was diluted to less than nine liters, say four liters, with water, the
20 solution rendered neutral but preferably faintly acid by the addition of acid, say hydrochloric acid, and then 200 grams or a similar amount of aluminum amalgam added. It may be noted that the potassium
25 carbonate may be neutralized with acid before the dilution with water. After standing for some time so as to allow the reaction to proceed, say one or two days, the aluminum hydroxid was filtered off. After filtering
30 the solution, the butylene glycol was recovered by evaporating off the water under reduced pressure. Other amalgams may be used and, further, the aluminum or other
35 metal or an alloy or several metals may be used and also without the use of mercury. In this condition the butylene glycol exists in a concentrated aqueous solution and is isolated by simple distillation, preferably under vacuum. This butylene glycol may
40 then be nitrated in any known way.

When I speak of glycerin trinitrate, of course I intend to include the glycerin mono- and-di nitrates, although I have shown only the formula of the glycerin trinitrate. In
45 like manner, when I use the term butylene glycol dinitrate I intend to include the buty-

lene glycol mono nitrate and the butylene glycol dinitrate, although I have only shown the formula of butylene glycol dinitrate.

Having now fully described my invention, 50 what I claim and desire to protect by Letters Patent is:—

1. The hereinbefore described method of producing butylene glycol, which consists in condensing acetaldehyde to acetaldol in the
55 presence of ice in contact with the acetaldehyde, adding an alkaline salt, gradually elevating the temperature during the condensing operation from substantially below 15°
60 C. to not above substantially 15° C., diluting the acetaldol solution with less than about 15 parts of water and adding an acid to render the resultant liquid approximately neutral but preferably slightly acid, and
65 then, without isolating the acetaldol, reducing the aqueous solution to butylene glycol by means of a metal amalgam.

2. The hereinbefore described method of producing butylene glycol, which consists in condensing acetaldehyde to acetaldol in the
70 presence of ice in contact with the acetaldehyde, adding potassium carbonate gradually in the form of a strong aqueous solution, gradually elevating the temperature during
75 the condensing operation from substantially below 15° C. to not above substantially 15° C., diluting the acetaldol solution with less than about 15 parts of water at a
80 temperature not above substantially 15° C., adding an acid to render the resultant liquid approximately neutral but preferably slightly acid, and then, without isolating the
85 acetaldol, reducing the aqueous solution to butylene glycol by means of aluminum amalgam.

In testimony of which invention, I have hereunto set my hand, at Philadelphia, on this 23rd day of January, 1911.

HAROLD HIBBERT.

Witnesses:

M. M. HAMILTON,

A. J. MAGUIRE,