UNITED STATES PATENT OFFICE.

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MANUFACTURE OF GLYCERIN NITRATES.

No. 830,909. Specification of Letters Patent. Patented Sept. 11, 1906.

Application filed January 5, 1905. Serial No. 239,732.

To all whom it may concern:

Be it known that I, ANTON MIKOLAJCZAK, a subject of the King of Prussia, German Emperor, residing at Kastrop, in the Province of Westphalia and German Empire, have invented new and useful Improvements in the Manufacture of Glycerin Nitrates, of which the following is a specification.

This invention relates to the manufacture of dinitroglycerin, as described and claimed in my application, Serial No. 203,762, filed April 18, 1904, on which United States Patent No. 798,436 was granted to me, and in my copending United States application, Serial No. 229,961, filed October 25, 1904, I have described a process of manufacturing explosives in which dinitroglycerin is used as a solving medium.

The present invention relates more particularly to a process whereby dinitroglycerin is manufactured in conjunction with trinitroglycerin in such proportions as to produce a mixture of di and tri nitroglycerin in which the former represents at least three per cent. of the nitroglycerins. Thereby a product is obtained which compared with other nitroglycerins shows certain advantages of essential importance, due to the presence of dinitroglycerin, the characteristic features of which have been more fully set forth in my above application, Serial No. 203,762, (United States Patent, No. 798,436.)

I found that with the aid of dinitroglycerin gunpowders and explosives generally can be manufactured which possess a high degree of stability, retain their plastic character and form, even during the coldest winters, and are in no wise inferior in force and effect to nitroglycerin explosives at present in general use, while by proper choice of the components they can be so manufactured as to afford safety against the ignition of fire-damp and coal-dust in mines. As the percentage of dinitroglycerin increases the tendency to freeze (characteristic of trinitroglycerin) diminishes, so that it is of great advantage in the manufacture of glycerin nitrate if the product contains a high percentage of dinitroglycerin. Thus, for example, a nitrate containing some twenty parts trinitroglycerin and thirty parts dinitroglycerin will not freeze even at the lowest winter temperatures. In the manufacture of nitroglycerin as at present conducted great importance is attached to the production of as pure a trinitroglycerin as possible. For this reason it is customary under the term "nitroglycerin" to mean trinitroglycerin. Any dinitroglycerin which may have formed unintentionally in the nitroglycerin is eliminated from the final product in the purifying (washing) process. As manufacturing materials it is customary to employ glycerin and a so-called "nitrating" mixture, consisting, for instance, of nitric acid and sulfuric acid (with or without the addition of other dehydrating substances) or of saltpeter and sulfuric acid.

The object of the process forming the subject of the present invention in contradistinction to prior methods is to obtain a product rich in dinitroglycerin. The new process consists in separating the oil from the charge as far as possible in order to avoid loss of dinitroglycerin, and this is done by adding subsequent to the nitration of the charge substances which wholly or partly neutralize the superfluous acid. Such agents are, for example, caustic alkalis and carbonates of the alkalies and alkaline earths.

In order to promote the production of dinitroglycerin in the charge, the proportions of glycerin and of nitric and sulfuric acids (which according to present practice are generally about one to three to five) may advantageously be altered, less sulfuric acid and, if desired, more glycerin being employed. In order that the dinitroglycerin formed in the charge may be the easier obtained, the quantity of water employed for the washing operation should be very small, while, on the other hand, the charge after each washing is allowed to stand for a considerable time in order that it may clarify.

As an example of manufacturing dinitroglycerin in mixture with trinitroglycerin directly I may cite the following: To sixty parts, by weight, of dynamite-glycerin sixty-four parts, by weight, of sulfuric acid (1.83° specific gravity) mixed with 127.5 parts, by weight, of nitric acid (1.50° specific gravity) are slowly added, and the mixture is stirred and kept cool at a temperature, by preference, below 26° Celsius. The mixture is then allowed to stand for half an hour, while the temperature is reduced, preferably, to 12° Celsius, whereupon the nitrated glycerin or oil can be separated from the acids. The said oil when sufficiently purified contains twenty-six per cent. trinitroglycerin and seventy-four per cent. dinitroglycerin, or the process may be carried out as follows: To one hun-

dred parts, by weight, of concentrated glycerin of 1.261° to 1.262° specific gravity a mixture of one hundred and eighty parts, by weight, of sulfuric acid of 1.795° specific gravity, and two hundred and fifty parts, by weight, of nitric acid of 1.5° specific gravity is slowly added, the whole being continually stirred and cooled meanwhile. Since the cold syrupy glycerin is difficult to agitate, it is advisable to first dissolve the one hundred parts of glycerin, while constantly stirring and cooling, in, say, ninety parts of nitric acid of 1.5 specific gravity. To prevent oxidation, the temperature of the mixture should be kept between + 10° and 15° centigrade. To this solution a mixture of one hundred and sixty parts, by weight, of concentrated nitric acid and one hundred and eighty parts, by weight, of sulfuric acid of 1.795° specific gravity (64° Baumé) is slowly added during continuous stirring, and by cooling the temperature is kept, if possible, below + 25° centigrade, or the one hundred parts, by weight, of glycerin may be first dissolved in the two hundred and fifty parts, by weight, of nitric acid, the mixture, if desired, allowed to stand for a time in order to complete nitration and the sulfuric acid then added. The charge is then diluted with cold water, and for the purpose of precipitating or eliminating therefrom the oil dissolved in the acid liquid the alkali—for example, carbonate of lime—or a solution of soda (about 30° Baumé) is added to it until the charge shows alkaline reaction. The oil may be separated from the aqueous liquid in the ordinary manner in a separatory funnel or other suitable apparatus, whereupon the oil is purified, as above set out.

The product thus obtained is one which, as will be seen, still contains a large amount of trinitroglycerin. The percentage of dinitroglycerin in the final product will, however, be the higher the smaller the quantity of sulfuric acid in proportion to nitric acid employed. Thus by suitably proportioning the nitrifying mixture with regard to the quantity of glycerin the percentage of dinitroglycerin and trinitroglycerin in the final product can be controlled, the degree of concentration of the reagents, the duration of the nitrating operation, and the temperature also exerting a certain influence, as is well known to those skilled in the art.

What I claim as my invention, and desire to secure by Letters Patent, is—

1. The process of manufacturing a mixture of glycerin nitrates containing dinitroglycerin and trinitroglycerin, which consists in reacting on glycerin with nitric acid in the presence of a dehydrating agent, in such proportions as are adapted to make dinitroglycerin, maintaining a low temperature until dinitroglycerin is formed in the acid solution, separating the dinitroglycerin by means of a neutralizing agent and removing the separated dinitrogylcerin with the trinitroglycerin.

2. The process of manufacturing a mixture of glycerin nitrates containing dinitroglycerin and trinitroglycerin, which consists in reacting on glycerin with nitric acid, in the presence of a dehydrating agent, in such proportions as are adapted to make dinitroglycerin, separating the dinitroglycerin held in solution and removing the separated dinitroglycerin with the trinitroglycerin.

3. The process of manufacturing a mixture of glycerin nitrates containing any desired proportion of dinitroglycerin and trinitroglycerin, which consists in reacting upon glycerin with nitric acid in the presence of a dehydrating agent, the relative proportions and concentration of the dehydrating agent, the nitric acid and the glycerin being such as to produce the desired proportions of dinitroglycerin and trinitroglycerin as described, and separating the dinitroglycerin from the solution in which it is held.

4. The process of manufacturing a mixture of glycerin nitrates containing any desired proportions of dinitroglycerin and trinitroglycerin, which consists in reacting on glycerin with nitric acid and a dehydrating agent, the relative proportions and concentration of the dehydrating agent, the nitric acid and the glycerin being such as to produce the desired proportions of dinitroglycerin and trinitroglycerin as described, and separating the dinitroglycerin from the acid solution by neutralizing the excess of acid.

5. As a new article of manufacture a nitroglycerin compound containing dinitroglycerin and trinitroglycerin, the former representing at least three per cent. of the nitroglycerins.

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses.

ANTON MIKOLAJCZAK.

Witnesses:

BERNHARD GRÄTZ,

CARL GARZ.