

UNITED STATES PATENT OFFICE.

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EXPLOSIVE.

SPECIFICATION forming part of Letters Patent No. 375,651, dated December 27, 1887.

Application filed July 25, 1887. Serial No. 245,251. (No specimens.) Patented in Germany April 20, 1886, No. 39,511; in France July 9, 1886, No. 117,309; in England July 14, 1886, No. 9,166, and February 21, 1887, No. 2,679; in Belgium August 2, 1886, No. 74,070; in Luxemburg August 5, 1886, No. 718; in Sweden August 7, 1886, No. 885, and in Norway August 19, 1886, No. 236.

To all whom it may concern:

Be it known that I, CARL ROTH, doctor of philosophy, subject of the Grand Duke of Hesse, and resident at Charlottenburg, near Berlin, Kingdom of Prussia, Germany, have invented certain new and useful improvements in the Manufacture of Explosives, (for which I have obtained Letters Patent in France July 9, 1886, No. 177,309; in Great Britain July 14, 1886, No. 9,166; in Belgium August 2, 1886, No. 74,070; in Luxemburg August 5, 1886, No. 718; in Norway August 19, 1886, No. 288; in Sweden August 7, 1886, No. 885; in Germany April 20, 1886, No. 39,511, and in Great Britain February 21, 1887, No. 2,679,) of which the following is a specification.

My invention relates to the manufacture of explosives from aromatic hydrocarbons and mixtures thereof, such as benzol, toluol, phenol, cresol, (cresylic acid,) and naphthaline, either derived from coal-tar or from other sources, fractional products of coal-tar in general, as also coal-tar itself; and it consists in combining with oxygen-yielding substances compounds prepared with said products by incorporating therein both chlorine and one or more nitro groups, and also in providing means for properly regulating the action of such explosives.

Of the carbon compounds which, when mixed with oxygen-yielding substances, form explosives, only the nitrated hydrocarbons and hydroxyl compounds of the aromatic group and certain sulpho-acids have hitherto been employed. (With reference to the nitro compounds as components of explosives, see "Sprengel on a new class of explosives which are non-explosive during their manufacture, storage, and transport," and the "Bulletin de la Société Chimique Française," 1873, XX, No. 10, p. 257, and with regard to the sulpho-acids see "Böckmann, Explosiv-Stoffe," p. 207, note.) No use, however, has heretofore been made for the same purpose of aromatic compounds containing both nitro groups and chlorine.

The advantage obtained by the introduction of chlorine as well as nitro groups into benzol, toluol, phenol, cresol, (cresylic acid,) and

naphthaline, fractional products of coal-tar in general, as also in the coal-tar itself, is that the chlorine exerts a loosening effect on the nitro groups, and accordingly enables the said groups to react more readily on the oxygen-yielding substances—that is to say, it enables the compound to burn more readily than when nitro groups only are present. As has been proved by numerous experiments, the dynamic effect is also considerably increased by the introduction of chlorine into the nitro compounds, probably in consequence of the increase in the volume of the combustion-gases by the chlorine when set free.

Compounds constituted as aforesaid, or mixtures of such compounds with each other, are obtained either by nitrating chlorated substances or by chlorating nitro products, or by the action of agents which produce a nitrating and a chlorating effect at the same time, preferably of a mixture of nitric and hydrochloric acids. And in order to give a guidance to those skilled in the art to which my invention relates, I will now proceed to describe as examples some ways of producing such aromatic chloronitro products.

First example: One part of benzol-chloride is gradually introduced into a mixture composed of three parts of highly-concentrated nitric acid of 1.52 specific gravity and six parts of concentrated sulphuric acid, the vessel being artificially cooled during the operation, if required, and after the evolution of nitrous vapor has ceased the reaction is completed by the application of heat. After the addition of water a crystalline product separates out, which, according to the degree of purity of the benzol-chloride, has a color varying between yellow and brown. This product is cleaved from the adhering acid by washing with a copious quantity of water, and afterward dried.

Second example: Chlorine is introduced into phenol, heated to 50° centigrade, until the weight is increased by one-half. The semi-fluid crystalline mass is then introduced in small portions into three times its weight of nitric acid of 1.4 specific gravity, the vessel being cooled during the operation. The

brownish product which is separated out by the addition of water is thereupon gradually introduced into a mixture of three parts of nitric acid of 1.52 specific gravity and five parts of concentrated sulphuric acid, and the reaction is completed by the heat of a water bath. A brown-yellow partially-fluid crystalline mass is thus obtained, which is washed and the moisture evaporated by a gentle heat.

Third example: One part of naphthaline is gradually introduced into a warmed mixture of five parts of nitrate of soda and six parts of concentrated sulphuric acid, and, after the most violent reaction is concluded, is gently heated with this mixture during three to four hours. One part of the washed yellowish-brown product having then been carefully mixed with 0.8 part of chlorate of potash, five parts of concentrated hydrochloric acid are allowed to flow by degrees into the mixture, and a gentle heat is applied to the vessel. The final product is freed from the adhering salt by washing with water, and dried, and then forms an easily-melting orange-yellow crystalline mass of about 1.4 specific gravity.

Fourth example: Twelve parts of nitric acid of 1.45 specific gravity are heated with four parts of sodium chloride during about one hour, to from 60° to 65° centigrade, and subsequently cooled. Two parts of naphthaline in small portions are then added to the mixture, and toward the conclusion of the reaction the whole is gently heated. The reddish mass which separates out, having been freed from salt by washing, is introduced into three parts of nitric acid of 1.52 specific gravity and six parts of concentrated sulphuric acid and digested with the acid mixture for several hours. The brownish-yellow product obtained after treatment with water is of a crystalline nature and of a specific gravity of about 1.4.

Fifth example: Four parts of the fractional distillate of coal-tar which goes over at a temperature of between 190° and 210° centigrade are gradually introduced into a mixture composed of ten parts of nitric acid of 1.4 specific gravity and five parts of hydrochloric acid of twenty-four per cent., the vessel being cooled during the operation. One part of the oily product, which after a time becomes crystalline, is gradually incorporated into a mixture composed of three parts of nitric acid of 1.52 specific gravity and seven parts of concentrated sulphuric acid, and the reaction is completed by heat. The product obtained, after washing and drying, forms a brown greasy mass, becoming crystalline at about 10° centigrade.

Sixth example: Five parts of coal-tar are caused to flow in a fine stream or jet into a mixture composed of fifteen parts of nitric acid of 1.45 specific gravity and twelve parts of hydrochloric acid at twenty-four per cent. After the more violent evolution of gas has ceased, the reaction is promoted by heat. One part of the plastic product of the reaction is

then introduced into a mixture of five parts of nitric acid of 1.52 specific gravity and fifteen parts of sulphuric acid and digested with the acid mixture for several hours. The final product obtained, after washing and drying, forms a brown amorphous powder.

The analysis of the product obtained according to the last example shows the proportion of chlorine contained therein to be 8.3 per cent. The proportion in the other products varies from ten to twenty-one per cent.

In order to produce the explosive matter, one part of the said chlorated and nitrated compounds is mixed, according to the quantity of carbon and of hydrogen present therein, with from two to five parts of oxygen-yielding substances, preferably with niter in its various forms—for instance, with nitrate of soda, of potash, or of ammonia. Especially powerful effects have been obtained with the mixture of one part of the chloronitro compound produced according to example four with two parts of nitrate of potash.

As before mentioned, explosives combined in the manner described possess the property of very rapid combustion in exploding, and, besides, require a strong flame or flash, such as that produced by fulminate of mercury. In order to render them fit for use where it is desired to have a less sudden or violent action, and, moreover, to permit them to easier explode, I may proceed as follows:

To the blasting-mixture consisting of chlor-nitro (chlorated and nitrated) products and substances yielding oxygen I add a small percentage of sulphur. This sulphur diminishes the suddenness or rapidity of the explosion, and, moreover, augments the "heaving" or splitting action on the one hand, and on the other increases the certainty and ease with which the charge can be exploded, and enables the compound to be exploded by ordinary powder, provided the charge be completely shut in or inclosed between solid walls, (being placed in well-tamped blast-holes, for instance.) Such an addition of sulphur is especially advantageous in the case of chloronitro products of benzol, toluol, phenol, cresol (cresylic acid,) and naphthaline with nitrate of ammonia as the oxygen-yielding substance. The quantity of sulphur to be added is regulated according to the amount of oxygen available in the oxygen-yielding component employed and according to the degree of facility with which the oxygen is given off. When nitrate of potash is employed as the oxygen-yielding substance, the quantity of sulphur to be added to the explosive mixture amounts to from about three to four per cent., by weight. The quantity of sulphur used may in some cases amount to as much as fifteen per cent. without depriving the compound of its explosive character. Such large proportions of sulphur are to be employed in cases where the explosive is required to partake more of the character of gunpowder, the action being of a propelling rather than of a splitting nature. When nitrate of am-

monia is used as the oxygen-yielding agent, a percentage of sulphur amounting to from about one to two per cent. of the total weight of the explosive mixture prevents the blasting-charge from producing an excessively disintegrating and pulverizing action in blasting coal, for example, and diminishes the waste in dust.

The most advantageous way of adding the sulphur is to melt it with the chlornitro products, as almost all these substances dissolve more or less sulphur and then retain it uniformly distributed throughout the mass when set or stiffened. When not convenient to melt the materials together, the sulphur is to be added to the other ingredients of the blasting-mixture in a finely powdered condition. The said chlornitro products can also be used in combination with simply nitrated aromatic compounds—such, for example, as nitro-benzol, dinitro-benzol, and the like—and mixed with oxygen-yielding substances. This method of employing the chlornitro products is not so suitable for the chlorated and nitrated coal-tar itself, but is more especially applicable with the chlorated and nitrated compounds of benzol, toluol, phenol, cresol, (cresylic acid,) and naphthaline.

The following are examples of blasting compounds of this description:

30 First. One part dinitro-chlorophenol; 0.5 part nitro-benzol; 0.5 part dinitro-benzol; two parts nitrate of potash; 2.5 parts nitrate of ammonia.

Second. One part picric acid; one part trinitro-chlornaphthaline; 2.5 parts nitrate of ammonia; 1.5 part nitrate of potash.

In the claims I employ the term "hydrocarbons of the aromatic series" to cover the class of substances referred to above, including such as benzol, toluol, phenol, cresol, (cresylic acid,) and naphthaline, whether derived from coal-tar or otherwise, or even coal-tar itself containing such substances as constituents.

I am well aware that aromatic hydrocarbons have been treated so as to incorporate therein both chlorine and nitro groups, and I therefore do not claim the processes described for that purpose in this specification; but

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

1. The new explosive which consists of the combination of a chlornitro-hydrocarburet of the aromatic series with an oxidant, such as a nitrate, substantially as set forth.

2. The improved explosive consisting of the combination of chlornitro-benzol with an oxidant, such as nitrate of ammonia, substantially as set forth.

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

CARL ROTH.

Witnesses:

H. SPRINGMA.

B. POL.