

UNITED STATES PATENT OFFICE.

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EXPLOSIVE AND METHOD OF MAKING SAME.

SPECIFICATION forming part of Letters Patent No. 598,618, dated February 8, 1898.

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To all whom it may concern:

Be it known that I, ERNEST AUGUSTE GEORGE STREET, of Paris, France, have invented certain new and useful Improvements in Explosives and the Manufacture of the Same, which improvements are fully described in the following specification.

Being aware of the serious drawbacks met with in the manufacture, handling, and use of chlorate powders hitherto known in connection with explosives, I have endeavored to describe a method of obtaining stable explosives containing chlorates so that the ingredients, whatever be their sensitiveness to shock and temperature, may be thoroughly mixed without danger.

The present invention relates to such explosives and to the process of their manufacture. Chlorate powders, like all explosives, must consist of substances providing for combustion, of the chlorate description, and of combustible substances, the proportions being such that when explosion occurs a complete combustion takes place, (carbonic acid or carbonic oxid.) It is necessary that the elements or ingredients constituting the explosive should be thoroughly combined or mixed with each other. Finally, it is necessary to render the substances to be combined harmless under shocks and high temperatures which may occur during the manufacture and handling of these explosives. I have found that in order to fulfil all these conditions it is necessary to render the combustible agent liquid during the whole process of manufacture. For this purpose I utilize the properties of certain oils to dissolve, when heated, nitro and azo compounds, which I choose in preference to all other combustible substances. If the solubility of the nitro or azo compounds in these oils be small, I use other substances which are more soluble and are formed by the combination of two nitro compounds or of two azo compounds or of one nitro and one azo compound. I use, preferably, the exact quantity of oil required to dissolve the combustible substance chosen. The oil itself plays the part of a combustible. But this quantity of oil must be sufficient to preserve the fluidity of the combustible mixture during the whole process of the manufacture, and this must be done in spite of the fact that the substance

will have to be suitably heated. The oily combustible mixture surrounds each grain of chlorate, the element providing for combustion, with a shell or coating of solid or paste-like combustible, so that when after the kneading the mixture is cooled there are formed crystals of nitro or azo compounds around the grains of chlorate. The existence of such shell is proved by the fact that in my explosives, having for their bases, say, chlorate of soda, this salt, usually hygrometric, is not influenced by atmospheric moisture. It must also be pointed out that the oil cannot exude.

The mixture is prepared at a very high temperature, so that when it is cooled and falls to the highest temperature occurring in summer the crystallization or the paste-like state is formed. The explosive obtained in this manner is so stable that it may be heated to 150° to 200° centigrade without its nature being in the least altered, and at the same time its effect when exploded is very powerful, owing to the combustible substances employed. These advantages disappear if chlorate and the nitro or azo compound combustible are simply mixed together and the mixture moistened by oil and not dissolved in it, as has been done with cold picric acid. It is found that oil exudes when the temperature rises. Besides, it will be easily seen that by the simple mixing an explosive of less density is obtained than when the material is dissolved in the oil.

Before describing the details of manufacture of these chlorates it is necessary to give some details about the substances I have selected as combustible agents in my explosives.

Nitro compounds.—The nitro compounds, which must not be confused with nitrated ethers, such as nitroglycerin and nitrocellulose, are divided into nitrohydrocarbons, (mononitrobenzene, mononitronaphthalene, dinitronaphthalene, trinitronaphthalene, bitrobenzene, &c.,) nitrophenols, (trinitrophenols, picric acid, tetranitrodiphenols, &c.,) and nitroamins, (nitroanilin, nitrated diphenylamin, &c.) They are insoluble or very slightly soluble in cold and hot mineral oils. They are little soluble in cold animal or vegetable oils, but are, on the contrary, soluble in different proportions in the latter category of oils if heated to a suitable temperature.

The following examples may be given:

Crude mononitronaphthalene melts at about 52°. If purified and sublimated, its fusion-point is 61°. At the ordinary temperature (from 15° to 20°) castor-oil dissolves about twenty-five per cent. of mononitronaphthalene—that is to say, one hundred parts, by weight, of oil dissolve twenty-five parts of mononitronaphthalene. From 65° upward this compound can be added in any proportion. The solubility in olive and linseed oil is practically the same as in castor-oil. A solution of equal parts of oil and a mononitronaphthalene solidifies when cooled.

Crude binitronaphthalenes, which are mixtures of binitronaphthalenes *A* and *B*, the respective melting-points being 240° and 170°, are but slightly soluble in castor-oil. At the ordinary temperature scarcely one per cent. dissolves. At 100° the solubility increases and reaches about four to five per cent. At 125° the solubility becomes about sixty per cent., while at the melting temperature of the nitro compounds (about 170° to 180°) the two liquids may be mixed in any proportions. The solution solidifies when cooled.

Crude binitrobenzene melts at about 70° and when pure at 90°. At the ordinary temperature its solubility in castor-oil is about four per cent., in olive-oil about three per cent., and in linseed-oil about five per cent. At 90°, the temperature at which binitrobenzene is completely liquefied, twenty grams of castor-oil and twenty grams of binitrobenzene mix perfectly and give a clear liquid which solidifies when cooled.

Picric acid or trinitrophenol liquefies at 125°. At the ordinary temperature linseed-oil dissolves about five per cent. of picric acid, castor-oil about four per cent., and olive-oil about one per cent. At 100° castor-oil dissolves about twenty per cent. of picric acid, and at about 125° to 130°, the temperature of fusion of picric acid, castor-oil does not dissolve more than fifty per cent. of picric acid. If a greater quantity is added, the picric acid forms a brown liquid layer under the oily solution of picric acid.

Azo compounds.—I have found, besides, that azo compounds—azobenzol, azoxybenzene, amidoazobenzol, diamidoazobenzol, &c.—have the same properties as nitro compounds. They are much more soluble in animal and vegetable oils when heated than when cold and mostly insoluble or but little soluble in mineral oils even when heated. Azobenzol and oxyazobenzol are, however, soluble in paraffin and vaseline when heated. Amidoazobenzol and diamidoazobenzol are less soluble.

Combinations of nitro and azo compounds between themselves.—By studying nitro and azo compounds it will be found that some of these substances are relatively little soluble in oil heated even to a high temperature. For instance, picric acid, as I have said, at 125° to 130° does not dissolve in castor-oil to

a greater extent than fifty per cent. These high temperatures cannot be used on a large scale in the manufacture of powders, as they would in certain special cases be extremely dangerous. Besides, even by heating under such conditions it will be found impossible, for instance, in the case of picric acid to dissolve in the oil a sufficient quantity of it. To obviate these drawbacks, I was led to study a whole class of substances produced by the combination of nitro or azo compounds between themselves, two and two, in order to use them instead of nitro or azo compounds, which are little soluble in the oils when heated. These combinations melt and become dissolved in oils at temperatures which are much lower than those at which their components dissolve. The incorporation of such combinative substances in oil can therefore be made without danger. It should be added that by using these binary combinations much more powerful explosives are obtained than when their components—the single nitro or azo compounds—are employed. These binary compounds may be prepared by the method generally used in chemistry by combining the components molecule to molecule and in the state of fusion. At first the substance is melted whose temperature of fusion is the lowest, and then the second substance is introduced into the liquid mass. By combining a substance, comparatively speaking, very fusible—such, for instance, as mononitronaphthalene—and a substance difficult to liquefy—such, for instance, as picric acid—a combination is produced the melting-point and the point of solution of which are much lower than that of picric acid. In case that the nitro compound is too unstable to be melted the nitro compounds are dissolved in oil one after another, beginning with the most soluble. The combination takes place directly in the oil. All the solutions of nitro compounds in oil can be, besides, obtained in this manner. Thus considerable quantities of combustible substances are incorporated in oil. Thus in one kilogram of oil only five hundred grams of picric acid can be dissolved at 125°, whereas if three hundred and forty-five grams of mononitronaphthalene have been previously dissolved in this kilogram of oil it will be afterward possible to dissolve at a temperature of 100° four hundred and fifty-five grams of picric acid and at 125° six hundred and forty grams of mononitronaphthalene and eight hundred and sixty grams of picric acid. We will, however, examine hereinafter in detail certain of these combinations as regards their melting and their solubility in oils. It is also easy to produce these combinations of nitro or azo compounds by dissolving the component substances in any solvent—ether, alcohol, acetone, chloroform, benzene, &c.—the solvent being got rid of by evaporation, leaving the combination, which can then be dissolved in oil.

The following are some details as to the

manufacture and melting-points and solubility of these binary combinations, which in my opinion are destined to play the chief part in the manufacture of chlorated explosives.

5 As an example, in order to obtain picronitronaphthalene one kilogram of mononitronaphthalene is introduced into a vessel heated by a water-bath or by steam to 90° or 100°. Then after it has melted one kilogram three hundred
10 and twenty grams of picric acid is added little by little. When the solution is complete, the whole is cast in plates. The combination is ready for use and melts at 74°. Without heat castor-oil dissolves about five per cent. of
15 this nitro combination. At 100° the solubility considerably increases, and castor-oil can dissolve ninety per cent. of picronitronaphthalene, which crystallizes when the solution is cooled and solidified. Being heated to about
20 105° to 110°, twenty grams of castor-oil can dissolve twenty, twenty-five, and even thirty grams of picronitronaphthalene. These two substances become capable of being mixed with each other. Other oils behave very much
25 like castor-oil. Linseed-oil is slightly attacked when hot.

Picrobinitrobenzene is prepared similarly to picronitronaphthalene. One kilogram of binitrobenzene and one kilogram three hundred and sixty grams of picric acid are taken,
30 the combination melting at 88°.

Castor-oil dissolves, when cold, six to seven per cent. of the combination. At 100° the solubility increases. The oil can dissolve
35 fifty per cent. of the nitro combination. By raising the temperature beyond 100° it will become possible to mix twenty grams of castor-oil and twenty grams of picronitrobenzene.

40 Picrates of amidoazobenzol, azobenzid, azoxybenzid, and nitrodiphenylamins have practically the same solubility in oil as the azo compounds used for their preparation. Picrate of diamidoazobenzol is, however, less
45 soluble than diamidoazobenzol only. These picrate azo compounds are prepared by dissolving at first the azo compounds in oil at the temperature of 80° to 100° and then adding picric acid in small portions. These so-
50 lutions once prepared may be heated to a point much higher than that at which the azo compounds decompose when heated alone. I have heated these solutions to 200° without
55 observing spontaneous decomposition or explosion.

Picramic acid can generally be substituted for picric acid.

New processes of manufacturing of chlorate powder.—In order to manufacture this
60 kind of explosive, the nitro or the azo compound is dissolved in the most suitable oil, heating it, if necessary, to the melting-point of the nitro compound as long as there is no danger of decomposition of the nitro com-
65 pound or of explosion during this increase of temperature. The nitro compound or the azo compound must dissolve in such proportions,

that when cooled down to the highest summer temperatures it will crystallize, bringing about solidification of the oily mass, or re-
70 main very paste-like in order to prevent exudation. If it were found that dissolving under such circumstances is impossible, or if in order to bring it about it were necessary to raise the temperature to the point of de-
75 composition of the nitro or azo compounds, then recourse may be had to a previous preparation, by the methods indicated above, of the combination the most soluble in oil of this nitro or azo compound with another nitro
80 or azo compound. Then, having obtained this binary compound, it would be dissolved in oil, as was the case for very soluble nitro compounds. The oily solution having been pre-
85 pared, it is poured out into a stirring or mixing apparatus and heated to a suitable temperature—say about 100°—in order to maintain perfect fluidity during the whole stirring operation. Then starch or carbon is added
90 and stirred till it is thoroughly absorbed or mixed with the oily solution. Then finely-pulverized alkaline chlorate or perchlorate is added little by little, the mass being constantly stirred. The complete kneading or
95 mixing operation, which is very short when a liquid combustible is used, must continue till the mixture is very complete. Then it remains only to fill the cartridges or to put up the material in the manner desired.

Generally speaking, it is found that a good
100 explosive should contain about ten to twenty per cent. of oily solution obtained as herein-before described, eighty to sixty-five per cent. of chlorate of an alkali, and ten to fifteen
105 per cent. of fecula, starch, or carbon. The latter substances may be dispensed with; but in such case the explosive should preferably be composed as follows: twenty to thirty per cent. of oily solution and eighty to seventy
110 per cent. of chlorate of an alkali.

The following are some examples which have been found to give good results:

Chlorate of potash, three kilograms; oily solution of nitronaphthalene, (in equal parts,) four hundred grams; starch, six hundred
115 grams.

Chlorate of soda, eight hundred grams; oily solution of picronitronaphthalene, (in equal parts,) two hundred grams.

Chlorate of soda, seven hundred and fifty
120 grams; oily solution of picronitronaphthalene, (in equal parts,) two hundred grams; starch, fifty grams.

Chlorate of soda, three hundred grams; azobenzol, seventy grams; castor-oil, thirty
125 grams.

Chlorate of potash, four hundred grams; picroazobenzol, sixty grams; castor-oil, forty grams.

To the latter two mixtures may be added
130 twenty to forty grams of starch.

Although perfect fluidity of the combustible nitro or azo compound is necessary during the whole operation (consequent to the

previous solution) in order to obtain good explosives, I also reserve to myself the right to manufacture detonation mixtures by using either nitro or azo compounds or binary combination formed by nitro and by azo compounds previously wetted, when hot, by animal, vegetable, or mineral oil and afterward mixed with an alkaline chlorate with or without hydrocarbons. As simply wetting is employed in this case, mineral oil may be used without inconvenience, as it is not intended to dissolve the combustible substance.

It has already been pointed out that the azo derivatives present the same or similar characteristics for the purposes of this invention as the nitro bodies and are the equivalents thereof. It will hence be understood that where nitro derivatives are specified in the claims as typical bodies the equivalent azo bodies are to be included. It will also be understood that in forming a compound combustible agent I do not restrict myself to two bodies only.

I claim—

1. The process of making explosives consisting in preliminarily dissolving in a suitable oil at an elevated temperature a combustible agent such as specified (such as a nitro derivative) in such proportion that on cooling the oily mixture will assume by crystallization a pasty or solid consistence, and then mixing with this solution alkaline chlorate or perchlorate, maintaining the fluidity of the mass during malaxation, substantially as described.

2. The process of making chlorate explosives consisting in combining a less soluble combustible agent with a more soluble combustible agent, dissolving this combination at an elevated temperature in a suitable oil, in such proportion that on cooling the mixture assumes a solid or pasty condition by crystallization, and then mixing with this solution the agent supporting combustion (chlorate or perchlorate) maintaining the fluidity of the mass during malaxation, substantially as described.

3. In the manufacture of explosives, the process of preparing a combustible solution for subsequent mixing with the agent supporting combustion, said process consisting in raising to a high temperature an oil which is not a solvent of nitro derivatives at ordinary temperature, and dissolving a nitro derivative in said heated oil in such proportion that, on cooling, the solution assumes by crystallization a solid or pasty condition, substantially as described.

4. The process of making chlorate explosives consisting in uniting at an elevated temperature the selected combustible agent (as a nitro or azo derivative or combination thereof) with an oil which is not a solvent thereof at ordinary temperature, and mixing the paste thus obtained with the chlorate powder, substantially as described.

5. An explosive whose combustible element is composed of a solution of a nitro derivative in an oil which is not a solvent thereof at ordinary temperature, substantially as described.

6. An explosive whose combustible element is composed of a solution in oil of the combustible agent (such as a nitro derivative) in crystalline condition surrounding or coating the grains of the element supporting combustion.

7. An explosive whose combustible element is composed of a solution in oil of a less soluble combustible body (such as a nitro derivative) combined with a more soluble body of the same class in crystalline condition, substantially as described.

8. An explosive, whose combustible element consists of a solution in oil of picric acid combined with a more soluble body of the same class, substantially as described.

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

ERNEST AUGUSTE GEORGE STREET.

Witnesses:

EDOUARD P. MACLEAN,
EDWARD BARBARY.