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EXPLOSIVE PERCHLORATES OF ALIPHATIC
NITROGENOUS COMPOUNDSWalter W. Vogl, Omaha, Nebr., assignor to Ralph
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10 Claims. (Cl. 52-1)

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Perchlorates have heretofore been used in explosives, e. g., mixtures of inorganic perchlorates with oxidizable materials, have been proposed. Also perchlorates of aromatic amines, have been proposed for use in explosives, but have not proven wholly satisfactory. The perchloric acid esters of glycol and of lower alcohols were investigated as explosives, but were too sensitive and were found to be too dangerous.

As the result of my researches, I propose the use, as explosive (alone or with oxidizable substances), of perchlorates of certain aliphatic nitrogenous compounds having two or more basic nitrogenous group and more than two carbon atoms, or perchlorates of derivatives of such compounds. Further my inventions cover processes for the manufacture and the purification of such explosives. No explosive of this kind has been described or used in practice until now. Many substances covered by this invention are outstanding explosives of highest potency which is in the order of magnitude of the energy of glycerine trinitrate. The other properties are much more favorable than those of the other explosives of highest energy and the velocity of detonation is very great. They are not objectionally sensitive to heat, mechanical impact, atmospheric conditions or electrical discharges. The lead-block test (modified Trauzl-test) showed that the blasting of explosives covered by this invention produces an enlargement of the borehole more than twice as large as that produced by the same amount of picric acid, ammonium picrate and trinitrotoluene. Some of the explosives covered by this invention have an excess of oxygen so that it is possible to increase the heat developed by the explosion by addition of oxidizable substances like carbon, metals, etc. Sometimes it is also possible to increase the velocity of detonation by addition of another explosive with a deficiency of oxygen, e. g. TNT. It is furthermore possible to manufacture some of the explosives covered by this invention in such a way that not all of the basic nitrogenous groups are linked to perchloric acid so that some of the basic groups are available for condensation or polymerization. Another important advantage of this invention is that the processes for the manufacture of these explosives are much easier and less dangerous than the processes of making the explosives now in use. Especially the process by double exchange reaction is very advantageous and economical because the use of free perchloric acid is avoided. The liquors produced by the electrolysis of metal

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chlorides containing the perchlorates of the metals may be used in the condition in which they are produced in electrolysis, or after suitable alteration in their concentration. If for

5 this process the dihydrochlorides or polyhydrochlorides (as they are produced by ammonolysis of alkylene-chlorides) are used as salts of the nitrogenous bases, and these salts are reacted with the solution of sodium perchlorate, the resulting sodium chloride may be redissolved and reused for electrolysis. The use of the perchlorates covered by this invention as explosives, is not limited to compounds which contain besides the nitrogenous groups, only carbon and
15 hydrogen (like the alkylene-diamines, the di- and poly-alkylene-polyamines), but includes also substances containing other elements or groups like the alkyl-oxides or sulfides with basic nitrogenous groups like diamino-diethyl-ether,
20 diamino-diethyl-sulfide, furthermore hydroxy-alkyl-alkylamines (with more than one amino group) amides of organic acids, carbamid and its derivatives, etc. Another advantage of most of the explosives covered by this invention is the
25 fact that they are very easy to purify even to the highest degree of purity. The raw materials for the explosives covered by this invention are available in the United States of America in practically unlimited quantities.

30 The following examples are given as illustration, without limiting the invention thereto:

Example 1.—To 200 kg. perchloric acid of about 50% strength (sp. gr. 1.402), 46 kg. of commercial ethylene-diamine are added with intensive stirring; the temperature of the reaction should be kept below 60° C. The resulting solution of ethylene-diamine-diperchlorate is then concentrated (in vacuo or under atmospheric pressure) until the formation of crystals starts,
40 i. e. until 90 kg. of water are evaporated. Thereafter the concentrated solution is cooled with or without stirring (depending on the size of crystals desired). The crystals are separated from the mother liquor and if desired, rinsed
45 with a saturated solution of pure ethylene-diamine-diperchlorate in water or alcohol, and dried in vacuo. If an alcoholic solution is used for the rinsing, a rinsing with ethyl ether may be applied thereafter and the crystals dried in a
50 current of air at 30° C. The ether may be recovered by absorption. The above mentioned mother liquor is taken up in strong ethyl- or methyl-alcohol, either in its original concentration or after concentrating it by evaporation
55 or by increasing its concentration by the addi-

tion of solid ethylene-diamine-perchlorate to be purified. The quantity of alcohol to be added to the mother liquor has to be such that the resulting alcoholic solution of ethylene-diamine-diperchlorate contains at least 80 parts of alcohol for 20 parts of water in the solution. To this solution, ethyl-ether or benzene is added, to precipitate the major part of the ethylene-diamine-diperchlorate, which is then separated from the liquid, rinsed with ether or benzene and dried. A third fraction of ethylene-diamine-diperchlorate may be obtained from the residue of the recovery of the organic solvents used in the process.

Example 2.—To 300 kg. of a watery solution, having a temperature of about 90° C., containing 100 kg. of propylene-diamine-dihydrochloride, 240 kg. of a 70% aqueous solution of sodium perchlorate is added and thoroughly stirred. Then ethyl alcohol is added in small portions until the solution contains at least eight parts of C_2H_5OH for each part of water in the solution, in order to precipitate the NaCl as crystals. After removing the crystals of NaCl the solution is evaporated to dryness. Any system of evaporation which is suitable for salt solution and in which the temperature of the parts in contact with the salt does not exceed 120° C. may be used. The solid residue is extracted with petroleum ether (or another solvent in which the propylene-diamine-diperchlorate is soluble but which does not dissolve the NaCl or the $NaClO_4$). After complete extraction, the remaining petroleum ether solution is separated from any propylene-diamine-diperchlorate which may have crystallized, and the solution in petroleum ether is extracted with water. The propylene-diamine-diperchlorate is thus transferred into a watery solution from which it is obtained in a manner similar to Example 1.

Example 3.—To 100 pounds of a 70% solution of barium perchlorate in water are added 25 pounds of ethylene-diamine in 50% water solution. After mixing, about 50 pounds of diluted sulphuric acid (35 degrees Bé.) are slowly added until no more precipitate is formed. The precipitated barium sulphate is separated and rinsed with water or diluted alcohol. The rinsing water or alcohol and the liquid containing the ethylene-diamine-diperchlorate are concentrated.

Example 4.—Ethylene-diamine carbonate in aqueous solution is treated with a 50% solution of perchloric acid, added in small portions until all carbonic acid is replaced by perchloric acid. At the end of the reaction it is advisable to raise the temperature of the solution almost to the boiling point. The end-point of the reaction is determined by methyl orange as indicator; any excess of acid has to be thoroughly neutralized either with ethylene-diamine base or with ethylene-diamine carbonate. To the neutral solution, for each 100 kg. of ethylene-diamine carbonate used, 10 kg. of strontium nitrate are added and after this dissolves the whole batch is evaporated in vacuo. The remaining solids are powdered and mixed with metallic magnesium in finest powder in the proportion of 30 parts of Mg for 100 parts of the said solids.

Example 5.—To diethylene-triamine in saturated solution at 20° C. in ethyl alcohol (50 vol. %), perchloric acid solution (e. g. @ 40% strength, sp. gr. 1.293) is added until the pink color of phenolphthalein which was added as indicator just disappears, i. e. until two of the basic nitrogenous groups are neutralized by the acid

but the third basic nitrogenous group remains free. The diethylene-triamine-diperchlorate is then precipitated by adding to the actual solution ten times its volume of a mixture of acetone and ethyl ether 1:1. The precipitate is removed and dried. To each 100 kg. of the dried diethylene-triamine-diperchlorate 25 litres of 40% formaldehyde solution are added and the mixture kept at 100° C. under reflux for 40 hours. Formaldehyde is given as an example of an aldehyde. The water and the surplus of aldehyde are thereafter removed by distillation in vacuo so that the product of condensation and/or polymerization remains as a mass which is plastic at higher temperature. With this plastic mass, 20% of diethylene-triamine-triperchlorate may be well incorporated in order to increase the velocity of detonation of the material. It will be observed that the triperchlorate has a higher ratio of oxygen to carbon and hydrogen than does the diperchlorate. If the mass has not the degree of plasticity required, some water-soluble plasticizer (e. g. 0.5% glycerol) may be added after 80% of the water has been removed by distillation, and then the evaporation completed.

Example 6.—100 kg. of ferric perchlorate ($Fe(ClO_4)_3$) are dissolved in 60 litres of water and to this solution 38 kg. of commercial ethylene-diamine are added slowly with stirring. Then the mixture is boiled and then filtered hot. The iron hydroxide cake is rinsed either with hot water or alcohol and the rinsing liquid added to the filtrate from which the ethylene-diamine-diperchlorate is obtained by one of the above processes.

Example 7.—To a mixture of ethylene-diamine and poly-ethylene-polyamine (a mixture which results in the ammonolysis of ethylene chloride) so much diluted perchloric acid is added that a proportion of all the basic nitrogenous groups present, equal to all the $-NH_2$ groups can combine with perchloric acid and a further proportion of all the basic nitrogenous groups equal to one-third of all the $=NH$ groups can also combine with perchloric acid. Then the solution is kept at 100° C. under reflux and with air bubbling through the liquid for 48 hours. During this treatment, the air may cause oxidation of some of the bodies present, to aldehydes and/or ketones, which may react similarly to the formaldehyde given above. Then the water is evaporated in vacuo. Should the resulting mass not have the desired plasticity some of the plastic explosive as described in Example 5, may be added.

These explosives are primarily intended for the filling of bursting missiles, like bombs, shells and torpedoes, but the easy regulation and the wide range of the velocity of detonation which is possible with these explosives makes them also very suitable for industrial blasting purposes and the slowest burning product may be used for fire works (signals, flares, etc.).

I claim:

1. An explosive containing as its essential constituent a perchlorate of a basic nitrogenous compound of an ethylenic hydrocarbon, said compound having more than two basic nitrogenous groups and of which a part only of the basic nitrogenous groups are combined with perchloric acid.

2. An explosive containing as its essential constituent a perchlorate of a propylene amine containing a plurality of basic nitrogen-hydrogen

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3. An explosive containing as its essential constituent a perchlorate of a polyalkylene polyamine which contains, per molecule, at least three basic nitrogenous groups, of which all but one are linked to perchloric acid.

4. A novel explosive, containing as its essential constituent a perchlorate of an alkylene polyamine, such alkylene compound containing at least two carbon atoms in a straight chain, and said amine containing —NH_2 groups and a =NH group, all but one of said nitrogenous groups, per molecule, being combined with perchloric acid and one of the said nitrogenous groups being combined with an aldehyde, such product being a plastic.

5. An explosive containing as its essential component a perchlorate of an aliphatic polyethylene polyamine in which at least one but not over one-third of the total number of basic nitrogenous groups contained therein remains free and all other basic nitrogenous groups are linked to perchloric acid.

6. An explosive containing as its essential component, a perchlorate of a polyalkylene polyamine, in which all but one of the basic nitrogenous groups are linked to perchloric acid, and in which one of the basic nitrogenous groups is reacted with an aldehyde to form a resin, and which explosive also contains an alkylene diamine perchlorate which contains a larger per-

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centage of perchloric acid radical than does said polyamine compound.

7. An explosive containing as its essential constituent, a dialkylene triamine perchlorate in which only two of the basic nitrogenous groups are united to perchloric acid and in which one basic nitrogenous group is not united to perchloric acid.

8. A polyalkylene polyamine perchlorate, in which at least about two-thirds of the nitrogenous groups contained therein are linked to perchloric acid and which compound also contains a basic nitrogenous group which is not linked to perchloric acid.

9. An explosive containing diethylene triamine diperchlorate plasticized by condensation with an aldehyde, and diethylene triamine triperchlorate.

10. An explosive containing as its essential constituent, a perchlorate of an alkylene amine, which compound has at least three basic nitrogenous groups and the alkylene groups of which contain at least two carbon atoms, and in which perchlorate at least two-thirds of the basic nitrogenous groups are combined with perchloric acid, such compound also containing a basic nitrogenous group which is not combined with perchloric acid.

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