

PATENT SPECIFICATION

185,555

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COMPLETE SPECIFICATION.



Initial Primers and a Process for their Manufacture.

I, Dr. HANS RATHSBURG, a citizen of the German Republic, of 25, Moststrasse, Fürth Bavaria, Germany, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The subject matter of the present invention is a process for the manufacture of new initial priming compositions. The disadvantages of mercuric fulminate are particularly its destructive action on aluminium, the ease with which it can be pressed to a "dead" state and also its uncertain action at the temperatures of liquid air and its low power of withstanding storage in the presence of moisture, and are sufficiently well known. Other initial explosives, which have recently been used as substitutes for mercuric fulminate, are also not without defects.

It has now been found, that the explosive salts of tetrazol (CH_2N_4) and its derivatives, are capable, by reason of their excellent properties of replacing mercuric fulminate and other initial explosives either wholly or partially, according to the purpose for which they are to be used. The principal ones which have been found to be of use for this purpose are; the alkali, earth-alkali and heavy metal salts of tetrazol (CH_2N_4), tetrazylazoimide or diazotetrazolimide (CHN_7), azotetrazol, ($\text{C}_2\text{H}_2\text{N}_{10}$), diazaminotetrazol ($\text{C}_2\text{H}_2\text{N}_{11}$), diazotetrazol (CN_6), bistetrazol ($\text{C}_2\text{H}_2\text{N}_8$), also the salts of phenyltetrazol - carboxylic - acid

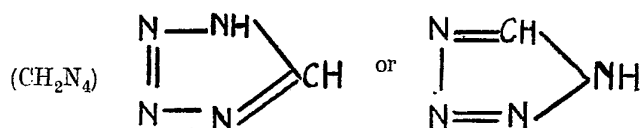
($\text{C}_8\text{H}_6\text{O}_2\text{N}_4$), methylmercaptotetrazol ($\text{C}_2\text{H}_4\text{N}_4\text{S}$), substituted dioxytetrazols such as phenylethenyl-dioxytetrazol ($\text{C}_8\text{H}_8\text{O}_2\text{N}_4$), β -naphthenyl-dioxytetrazol ($\text{C}_{11}\text{H}_8\text{O}_2\text{N}_4$), phenyl-glycolenyl-dioxytetrazol ($\text{C}_8\text{H}_8\text{O}_3\text{N}_4$), also benzenyldioxytetrazol ($\text{C}_7\text{H}_6\text{O}_3\text{N}_4$), meta-nitrobenzenyldioxytetrazol ($\text{C}_7\text{H}_5\text{O}_4\text{N}_5$), para-tolenyldioxytetrazol ($\text{C}_8\text{H}_8\text{O}_2\text{N}_4$) and similar derivatives and substitution products of tetrazol.

Instead of tetrazol there may be employed the salts of durable triazol, such for instance as are mentioned for example in Beilstein's "Handbuch der organischen Chemie" 3rd. edition, 4th vol. p. 1098.

Some tetrazol salts have already been known for a long time and have been described for instance in Beilstein's "Handbuch der organischen Chemie" 3rd. edition, 4th vol. p. 1333 and 1493, and also in the "Annalen der Chemie" vol. 270, p. 60 and vol. 273 p. 151. British Specification No. 2194/1892 also deals with the manufacture of so-called diazoguanidine (carbamidimidazide) and amidotetrazol. The salts however of both these latter compounds have no explosive character and cannot therefore come into consideration as a blasting and ignition medium for munition purposes (see also Beilstein's "Handbuch der organischen Chemie" 3rd edition, vol. 1, p. 1496).

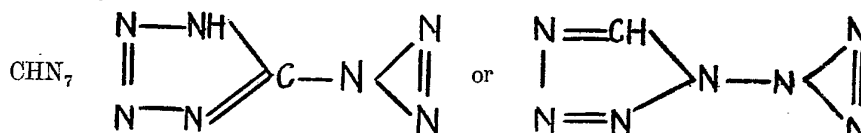
As some of the above referred to substances are of recent discovery I will make a brief reference to their structural diagrams and a method of manufacturing the same.

1. Tetrazol:



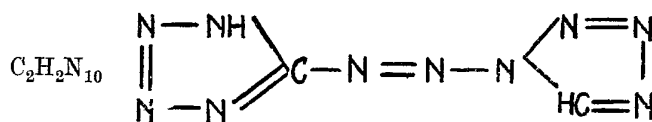
Tetrazol is obtained either synthetically from diluted hydrazoic acid and prus ic acid or by a reduction of diazo-tetrazol salts by chloride of tin or by alcohol, or finally by oxidation of a number of organic compounds with permanganate of potassium for instance of naphtyltetrazol or of aminophenyl-tetrazol. 10

2. Tetrazylazoimide or diazotetrazol imide:



Tetrazylazoimide or diazotetrazolimide from amidoguanidine salts and alkali nitrites. Tetrazylazoimide could be 20
15 or its salts are preferably prepared by splitting or cracking tetrazenes with rectilinear chain of the type $-\text{N.NH.NH.N}-$ with lyes, such (a tetrazene) could be obtained for instance further obtained by treating tetrazyl-hydrazine with sodium nitrite and hydrochloric acid.

25 3. Azotetrazol:

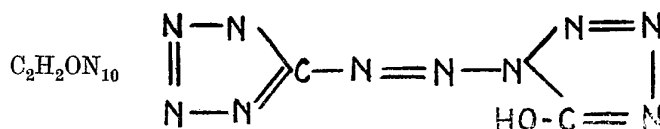


Azotetrazol and salts are prepared by oxidising amidotetrazol in alcohol solution with permanganates, persulphates and the like. 30

The amidotetrazol required is prepared either synthetically from cyanamide and

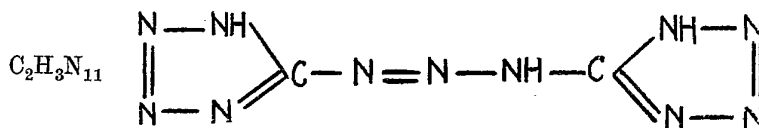
hydrazoic acid or by reconstitution in the presence of sodium acetate of guanlyl-azide salts which are obtained in diazotising amidoguanidine salts; the guanlyl-azide salts need not be isolated.

4. Oxyazotetrazol:



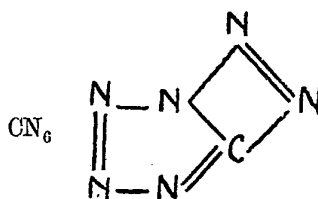
35 Oxyazotetrazol and salts are prepared by treating diazotetrazol salts with carbonic acid.

5. Diazoaminotetrazol:



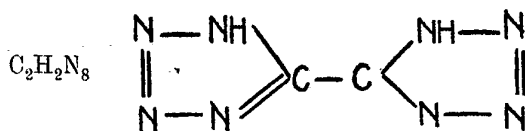
40 The manufacture of diazoaminotetrazol and its salts is effected in a simple manner by diazotising amidoguanidine salts with sodium nitrite in acetic acid solution.

6. Diazotetrazol:



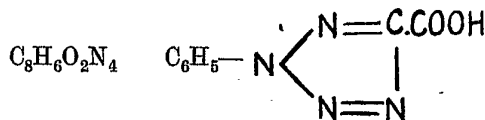
Diazotetrazol salts are obtained by diazotising amidotetrazol.

7. Bistetrazol :



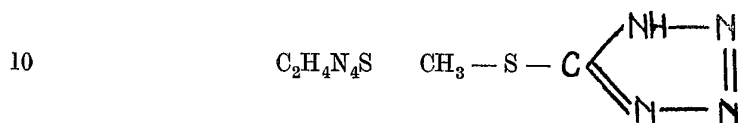
Bistetrazol and its salts are obtained synthetically from cyanogen gas and hydrocyanic acid solution.

5 8. Phenyltetrazol-carboxylic-acid.



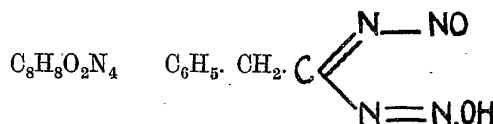
Phenyltetrazol-carboxylic-acid is prepared by boiling phenyl-tetrazol-cyanide with alcoholic potash lye.

9. Methyl-mercapto-tetrazol :

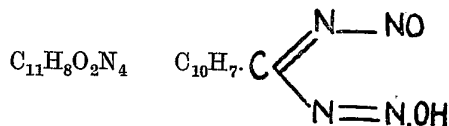


Methyl-mercapto-tetrazol is obtained by diazotising methyl-thio-semi-carb-azide.

10. Phenylethenyl-dioxy-tetrazol :

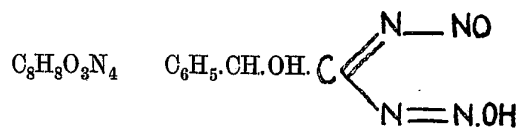


15 Phenylethenyl-dioxi-tetrazol salts are obtained by decomposing with alcoholic potash lye the phenyl-acet-amidine-salt thereof obtained during the diazotising of phenyl-acet-amidine-nitrate.

11. β -naphthenyldioxytetrazol :

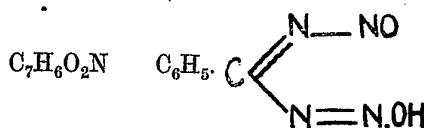
20 β -naphthenyldioxytetrazol is prepared in the same way by decomposing β -naphthenyl-amidine-salt obtained in diazotising β -naphthenylamidine.

12. Phenyl-glycolenyl-dioxy-tetrazol :

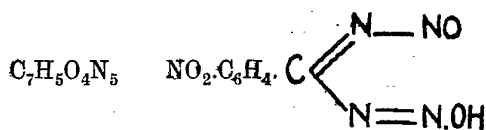


25 Phenyl - glycolenyl - dioxy - tetrazol. Manufacture by the decomposition of phenyl-glycolenyl-amidine-salt obtained by diazotising phenyl - glycolenyl-amidine.

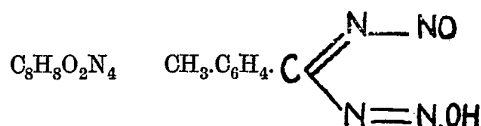
13. Benzenyldioxytetrazol :



30 Benzenyldioxytetrazol is prepared by diazotising acid benzenyl-amidine and decomposing the benzenyl-amidine-salt thus obtained.

14. *m*-nitro-benzenyl-dioxy-tetrazol :

m-nitro-benzenyl-dioxy-tetrazol is prepared by diazotising *m*-nitrobenzenyl-amidine.

5 15. *p*-tolenyldioxytetrazol :

p-tolenyldioxytetrazol is prepared by diazotising *p*-tolenylamidine and decomposing the resulting *p*-tolenylamidine-salt with alcoholic potash lye. 55

The salts of these tetrazol compounds possess in comparison with the known initial compounds and means of ignition various advantages. In particular they possess an extraordinary power of enduring storage. It is known from the literature on the subject alone that the tetrazol ring is exceedingly stable in its behaviour towards oxidising agents and is only split up at high temperatures by concentrated mineral acids. The heavy metal salts of tetrazolimide for example are almost not attacked at all even by strong acids and likewise by strong caustic lyes in contradistinction to the ease with which the azides of the heavy metals are attacked. 60

These explosives which possess the property of withstanding high pressures when treated in presses and of yielding firm compressed products, may be used with advantage for example in blasting detonators admixed with each other or also with known explosives or priming constituents as a top charge. 65

As an illustrative example for the filling of blasting detonators a charge of 70

40	1.00 gram tetranitromethylaniline (tetryl)	55
	0.15 „ lead or cadmium tetrazylnitride.	
	0.15 „ lead azotetrazol	

may be cited. 75

An increase in the safety of manipulation in conjunction with the extraordinary power of penetration of these tetrazol compounds can be effected in the well known way for example by granulating them with paraffin or resins dissolved in benzol, xylol, carbontetrachloride and the like with the addition, if necessary, of cork meal. 80

The initial priming action of the smallest quantities of the most shatter- 85

ing of these compounds, for example the tetrazyl nitrides, has hitherto not been determined. It has been found that even one to two milligrams of these substances are sufficient to completely detonate nitropentaerythrite. They therefore surpass mercuric fulminate to quite an extraordinary degree in their initial action. Other tetrazol compounds, such as the salts of azotetrazol, possess an advantage over the known priming explosives inasmuch as they are coloured a distinct yellow without possessing any colouring power of their own. They surpass in penetrative power salts of known nitro compounds, such as trinitroresorcinate of lead amongst others, which have the disadvantage both for the purposes of manufacture and that very little change of colour occurs which is inconvenient. 70

The use of the tetrazol compounds for the manufacture of primers is completely new. Even in the literature on the subject mostly only the alkali salts and the silver salt are described, while the most important ones for practical purposes are principally the lead and cadmium salts. 80

In order to combine the good properties of different compounds, such for example as sensitiveness to ignition, efficient transmission of flame, higher specific gravity, etc., and in this way obtain homogeneous priming compositions both for percussion caps and Flobert ammunition as well as for blasting detonators, it has been found to be advantageous to mechanically mix the salts of the said tetrazol derivatives not only with other explosives which are applicable in the present case, but to precipitate them together from solutions or to crystallise one salt on to the other, so that combinations of salts of the mixed crystal and double salt types are obtained. Suitable explosives of this kind are the diffi- 85

cultly soluble salts of azoimide, of mono- and polynitrated phenols and their substitution products, such as those of di- 90

- and trinitroresorcin, trinitroresorcin and trinitrochloroglucinol, for example. Salts of other compounds, which possess suitable properties for the above priming compositions, are also suitable for the production of such mixed crystals and homogeneous priming compositions, such for example as those of meta-dinitro-ortho - dinitrosobenzol and trinitro-dinitroso- β -naphthol.
- Having now particularly described and ascertained the nature of my said invention, and in what manner the same is to be performed, I declare that what I claim is:—
1. A detonator, blasting detonator, percussion cap or the like having an initial priming composition partially or wholly comprising an explosive salt of tetrazol or triazol or one of their derivatives.
 2. An initial priming composition for detonators, percussion caps or the like comprising one or more explosive salts of tetrazol or triazol compounds or their derivatives mechanically mixed or crystallised out with another explosive constituent.
 3. An initial priming composition comprising a composition as included in Claim 2 and having admixed therewith a phlegmatising agent.
 4. In a process for the manufacture of priming compositions, the partial or complete replacement or substitution of the usual mercuric fulminate by one or more of the explosive salts of tetrazol or triazol or their derivatives.
 5. An initial priming composition for detonators, blasting detonators, percussion caps and the like prepared or constituted in accordance with the last preceding claim.
- Dated this 27th day of June, 1921.
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