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J. TAYLOR

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SAFETY BLASTING DEVICE AND METHOD

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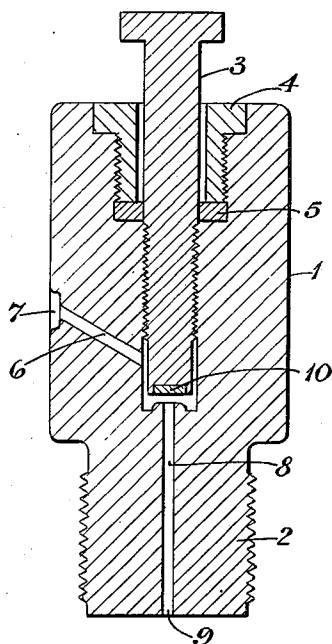


Fig. 1

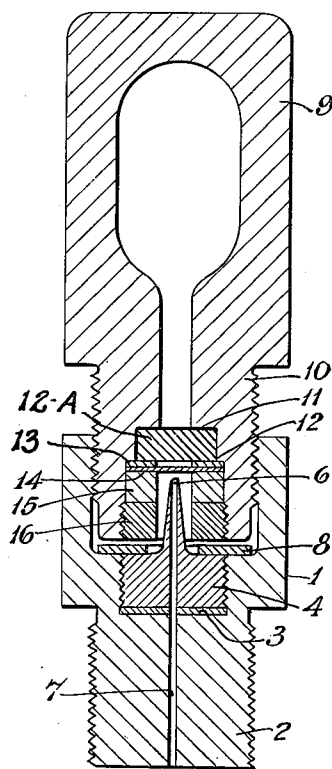


Fig. 2

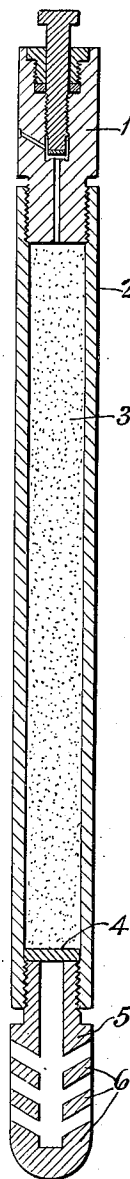


Fig. 3

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UNITED STATES PATENT OFFICE

2,255,602

SAFETY BLASTING DEVICE AND METHOD

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In Great Britain December 13, 1937

24 Claims. (Cl. 102-6)

This invention relates to blasting and blasting devices and more particularly to a method of blasting in which the blast is initiated without the use of a fuze or an electrical igniter.

It is known to use a blasting device which comprises a pressure-resistant metal vessel adapted to release gases generated therein at a sufficient pressure to cause a blasting effect in the borehole, with a charge capable of undergoing a self-sustained decomposition and comprising a mixture of an alkali metal nitrite with one or more ammonium salts, together with suitable initiating means.

Such a device requires some form of local heater to initiate the self-sustained decomposition of the charge, i. e. an electric detonator, a safety electric igniter of the totally enclosed or squib type or an electric powder fuze. All of these are capable of use even in fiery or dusty mines, in which such blasting devices find their principal application, but electric powder fuzes have the disadvantage that they must be loaded into the blasting device outside the mine. Apart from the nature of the local heater, however, there remains inherent risk of ignition by spark associated with electrical igniting systems, the existence of which is recognised in certain countries in the form of working regulations and particularly as affecting the kind of exploder permitted for use in fiery or dusty mines.

It has also been stated that the reaction



is accelerated by the presence of nitrous acid and also that self-sustained decomposition can be initiated in an aqueous solution containing an alkali metal nitrite and an ammonium salt confined in a blasting device, by the agency of a strongly acidic substance. The initiation of self-supporting decompositions in solid mixtures of these ingredients is however an entirely different problem from the initiation of such decomposition in solutions, and the mere addition of any strongly acidic substances to a solid mixture fails to initiate the self-supporting decomposition leading to the formation of nitrogen, an alkali metal salt and water more frequently than it succeeds. Such a state of affairs gives rise to grave dangers, if used in practice, as it may easily happen that the blast will not take place until men have returned to the face under the assumption that the blast has failed.

This invention has as an object to devise a method whereby a metal nitrite-ammonium salt blasting charge can be initiated without the use of any electrical heating device. A further object

is to devise a blasting apparatus to operate with a metal nitrite-ammonium salt charge in which the charge can be initiated without the use of any electrical device. A still further object is to devise such a method whereby the initiation will take place instantaneously or after a predetermined period of time and before the expiration of a further predetermined period. Further objects will appear hereinafter. These objects are accomplished by the following invention.

I have found that I can initiate the decomposition of a confined alkali metal nitrite-ammonium salt mixture so as to develop a blasting pressure within a pressure resisting metal vessel if I introduce into contact with a portion of the mixture a liquid acidic medium of at least one molar normal concentration capable of continuously regenerating hydrogen ions as it is consumed so as to maintain an alkali nitrite decomposing hydrogen ion concentration, the original pH of the acid solution being less than that of 0.7 normal hydrochloric acid solution.

This invention can be applied (1) to stable mixtures of alkali metal nitrite and ammonium salt, i. e. mixtures whose rate of decomposition on standing is so slow that it can be disregarded in all ordinary practice, (2) to unstable mixtures, i. e. mixtures whose rate of decomposition must always be taken into account when considering matters of storage and transport, and (3) to stabilised mixtures, i. e. mixtures which would normally be unstable but to which have been added stabilisers such as soda ash or magnesium oxide. For the purpose of this specification and claims when I refer to a stabilised mixture I refer to a mixture containing such alkalinity as to bring the pH of a saturated solution to at least 6.5.

The acidic medium may for instance be introduced into a charged steel tube blasting device by means of a screw capsule holding a small quantity of the acidic medium under pressure of dissolved gas, sealed by means of a diaphragm adapted to be ruptured on screwing the capsule home, or the acid medium may be forced in through a non-return valve by fluid pressure applied from a distant situation.

I prefer to define the maximum hydrogen ion concentration with reference to hydrochloric acid solutions as in practice the easiest method of establishing the feasibility of using an acidic medium is probably by comparative colour tests with an indicator using the 0.7 normal HCl solution as a standard. In the preferred form of my

invention I would use 0.5 normal HCl as the standard. Expressed in terms of pH, the maximum hydrogen ion concentration which I may use corresponds to a pH of .25 while I prefer to work with a pH greater than unity.

The minimum hydrogen ion concentration of the acidic solution usable may vary with the amount or nature of the stabiliser if present, and with the nature of the constituents of the solid mixture, but is governed by the condition that the concentration of hydrogen ions in the solution should remain sufficient to maintain a substantial rate of transformation of the material. Direct observations with dilute acids are not well adapted in practice to indicate the variety of choice available amongst materials of high pH value but by the use of buffered acid solutions, to which this objection does not apply, I have found that in the case of stoichiometric mixtures of sodium nitrite and ammonium chloride unstabilised and stabilised respectively with 2% soda ash and 1.5% magnesium oxide, the maximum permissible pH is respectively about 5.9, 5.2 and 5.2. For stoichiometric mixtures of potassium nitrite and ammonium chloride made without a stabiliser the maximum pH is about 4.3.

As liquid acid media for the purpose of the invention, there may be employed freely soluble weak acids generally, if their dissociation constants are not lower than about 10^{-5} at 15°C ., certain highly soluble strong monobasic acids, but only when in a concentrated state; certain highly soluble strong dibasic acids, in which both the dissociation constants are high, but only when in a concentrated state; dibasic acids and polybasic acids having at least one low dissociation constant; compatible mixtures of strong and weak acids; certain acid salts of di- and polybasic acids; certain hydrolysed salts having an acid reaction, and various buffered solutions. The above figures for the maximum permissible pH may be employed as a guide in the selection of very weak acids, acid reacting hydrolysable salts and buffered weak acid solutions if these are to be used. In the case of the salts the possibility that the reaction product of the salt with the ammonium salt present in the mixture might yield a different pH from that of the salt introduced or might react to form an insoluble product with one of the constituents of the mixture should not be lost sight of. The first mentioned of these possibilities would account for one or two instances in which salts of slightly higher pH than that indicated by buffered solutions as the maximum, have been effective. The divergences in maximum permissible pH between the different kinds of solid mixture are not surprising in the light of the varying alkalinity of the mixtures in question, but are only of practical significance in the case of acid reacting hydrolysable salts, acid salts and buffered solutions. If the acid medium employed is a simple acid in order to effect initiation of the contacted mixture, a higher concentration of the acid than would yield this pH must be used.

Among the acid salts that may be used there may be mentioned dihydrogen ammonium phosphate and sodium dihydrogen phosphate.

Among the hydrolysable salts of acid reaction there may be used zinc chloride, zinc sulphate, aluminium sulphate, copper sulphate and ferric chloride. Sodium, potassium, and ammonium dichromate give long delay periods of about $\frac{1}{2}$ hour with a mixture of sodium nitrite and ammonium chloride stabilised with 2% sodium carbonate and

granulated. Magnesium chloride, magnesium sulphate, manganese sulphate, ferrous sulphate and lead nitrate are not effective. Zinc nitrate and sulphate are not effective with powdery mixtures stabilised with $1\frac{1}{2}\%$ magnesium oxide, nor are copper sulphate or ammonium dichromate.

Among the buffer solutions available are mixtures of acetic acid with sodium acetate; and ammonium phosphate with di-ammonium hydrogen phosphate.

The maximum permissible hydrogen ion concentration of the acid medium used is governed by the condition that a substantial fraction of the nitrous acid that may be regarded as independently intermediately generated must be maintained in the oxidation state of nitrous acid. In the case of strong acids with unstabilised mixtures, I have found that the limit corresponds approximately to the hydrogen concentration of a 0.7 normal solution of hydrochloric acid, but already at a normality of 0.5 there is clear evidence of failure to maintain the nitrous acid state of oxidation. Under open conditions this evidence is visible, and consists in the plentiful appearance of brown fumes.

It is thus desirable in the case of the stable alkali metal nitrite-ammonium salt mixture to employ solutions in which the pH is substantially higher than that represented by a 0.7 normal solution of hydrochloric acid, whatever the type of acidic medium.

While the application of the principles referred to above provides for any given mixture an excellent choice of materials which may be used for the purposes of the invention, it is desirable to carry out a preliminary test of the material selected in accordance with these principles with a quantity of the stabilised mixture in a metal vessel open at one end; so that if necessary any adjustment of the material that may be required to accelerate or delay the onset of self-sustained reaction, or even a change to another acid medium, may be made. The times of delay experienced under open conditions are not very different from those experienced under closed conditions at the same temperature. It is not claimed that initiation can be brought about with certainty at temperatures below about 5°C ., but commercial blasting operations in coal mines do not call for initiation at such low temperatures.

For the purpose of carrying out the test, vessels such as those described in the succeeding paragraph are very convenient. The onset of self-supporting decomposition is very easily recognised by the large amount of steam generated, and may be easily distinguished by anyone who has witnessed it from the relatively slight thermal effects associated with the mere neutralisation of the stabiliser, or certain other reactions, to which reference will be made hereinafter, leading to the production of brown fumes.

By way of illustration of the difference in behaviour between a solid unstable mixture and a solid stabilised mixture, there may be quoted the following observations of the results obtained by the simple addition of 10 ccs. of various acid solutions to about 150 gm. of the mixture respectively to an unstabilised mixture in equimolecular proportions of sodium nitrite and ammonium chloride and to a similar mixture stabilised with 2% soda ash and granulated to pass a 4 and be retained on a 24 mesh B. S. S. sieve. The tests made were made at about 15°C . in open steel tubes, of $1\frac{1}{4}$ " internal and $1\frac{3}{4}$ " external diameter.

Liquid acidic media which under these conditions bring about the onset of the self-supporting decomposition of the mass within an induction period up to quarter of an hour are regarded as definitely useful for the purpose of the present invention, and unless otherwise stated in the following observations it is to be understood that a positive result indicates the initiation of self-sustained decomposition throughout the mass within this time. A failure, however, is reported if no initiation takes place after three-quarters of an hour.

Unstabilised mixture

The mixture may be initiated by dilute solutions of acids of very varied description, there being always some range of normality between 0.1 and 0.7 N at which the dilute acid is effective for initiation. The acids which may be used include strong monobasic acids such as hydrochloric and nitric, weak monobasic acids such as glycollic, acetic and butyric, and monobasic acids of moderate strength like monochloroacetic and trichloroacetic; strong and weak dibasic acids such as sulphuric, chromic, oxalic, tartaric, maleic and succinic; and tribasic acids such as phosphoric and citric. Phenol however fails. Hydrochloric acid and trichloroacetic acid fail at any normality above about 0.7 N although chemical reaction proceeds with evolution of brown fume and heat. Weak monobasic acids and weak dibasic acids and tribasic acids on the contrary succeed over the whole range of these higher normalities. With the strong or moderately strong dibasic acids and the monobasic acids of moderate strength in some instances, such as the case of oxalic and trichloroacetic acid, there is failure at all higher normalities; while with others such as sulphuric, chromic, tartaric and monochloroacetic acid immediately above the range already referred to at which they succeed there is a range of normality at which failure occurs, followed by a range of still higher normality at which they again succeed. This is also true for nitric acid. This upper operative range in the case of sulphuric acid extends from about 30% concentration upwards, in the case of monochloroacetic acid from about 33% upwards, and in the case of nitric acid from about 65% upwards.

This seemingly anomalous behaviour is probably due to the fact that with simple strong acids the hydrogen ion concentration rises to a peak as the concentration of the acid is increased, and then, if they are sufficiently soluble, it falls away again. If the acid concentration is sufficiently high the hydrogen ion concentration will have fallen away until it is again within the pH range which will initiate the reaction I require.

The minimum effective normality in the case of acetic acid, succinic acid and similar weak acids is about 0.1 normal.

2% soda-ash-stabilised mixture

In no case does a strong or moderately strong monobasic or dibasic acid with a high second dissociation constant initiate a self-sustained reaction communicating itself through the mixture, unless it is highly soluble, and those which succeed do so only at high concentration. Copious brown fumes are produced by a considerable range of concentrations lower than those that are effective, and brown fumes may be observed even when effective concentrations are used. Thus hydrochloric, trichloroacetic and oxalic acids fail at all concentrations, while monochloroacetic, sulphuric and nitric acids succeed only at con-

centrations of about 55%, 40% and 98% and upwards respectively. Chromic acid is very effective in concentrations from about 10% upwards.

Weak monobasic and dibasic acids and tribasic acids, whether dilute or concentrated, succeed; but the minimum normalities required are higher than for the unstabilised mixture, not usually being less than about 1.0 normal for acetic acid and tending to rise in the case of somewhat stronger weak acids. Weak acids of very low solubility accordingly fail. Compounds of exceedingly low dissociation constant, such as glucose and the like, also fail.

These results contrast strongly with the fact that the addition of 35% hydrochloric acid to about 23 times its volume of saturated solution of 2% soda ash stabilised sodium nitrite-ammonium chloride mixture brings about a long continued evolution of nitrogen with a progressive rise in temperature even though copious brown fumes are also evolved initially.

The results of the tests of the stabilised and unstabilised solid mixtures indicate that the problem of initiation is one closely connected with the strength of the acid, a term which is used herein in its ordinary sense with reference to the magnitude of the dissociation constant. Assuming that the volume of the mixture contacted by the acid is roughly proportional to the volume of acid introduced, from the fact that the possibility of a self-supporting decomposition depends on the heat evolution in the contacted volume exceeding the heat losses in and from that volume, one would expect larger quantities to be more effective, since the heat losses from the larger volume of mixture contacted would be relatively less severe than from the smaller. The above effective lower limits of normality refer to the use of 10 c.c., a quite arbitrary volume of acid, and would be somewhat higher if smaller volumes were employed. Obviously for practical purposes it would not be satisfactory to introduce a volume of liquid constituting any large fraction of the total volume of the charge, but it will be understood that somewhat larger volumes than 10 c.c.s. would be permissible. But when the acid is used at normalities slightly higher than the quoted lower limits quite considerable reductions can be made from 10 c.c.s. before failure ensues, and by adjusting the exact concentration of the acid in relation to a fixed volume used it is possible to control the delay in the induction of the propagation throughout the charge.

The facts indicate that with particularly effective normalities, only a very small amount of acid need be introduced and consequently that only a very small volume of the solid mixture need be contacted. The granulated mixture stabilised with 2% sodium carbonate is somewhat less sensitive to initiation by exceedingly small volumes of acid than the powdery mixtures stabilised with 1½% magnesium oxide, but only a drop or two of 15% phosphoric acid is required for the former and 0.03 c. c. of 50% acetic acid for the latter. It is also true that in effective cases quite a small total quantity of acid is required even when the dilution of the acid is substantial and the stabilizer is therefore capable of diminishing considerably the amount of acid available for the required purpose. Thus 5 c. cs. of acetic acid at a normality as low as about 1.5 are effective with a soda ash stabilised mixture.

On the other hand, acetic acid is ineffective at a normality below about 1. The conversion of

the stabilizer into metallic acetate at least partly accounts for the much higher concentration of acetic acid required for the stabilised than for the unstabilised mixture: but in the case of hydrochloric acid and similar strong acids for which a corresponding increase in concentration required by the alkalinity of the stabiliser would be expected, the failure to initiate must be ascribed to the fact that already at a concentration of 0.7 normal the pH of the strong acid introduced is sufficiently low to exert some strongly adverse influence on the course of the decomposition.

The following series of examples have been designed to investigate the delay between the time of adding the acidic substance to the metal nitrite-ammonium salt mixture and the commencement of self-propagating reaction.

In each case the mixture used was of sodium nitrite and ammonium chloride stabilised with 2% of sodium carbonate. The mixture was granular and placed in circular iron vessels about 1½" in diameter and about 4" high, being open at the top.

To these were added various acidic substances at various temperatures and the results are given in the following table in which the first column gives the temperature, the second column the time delay when the acidic substance is 15 gms. of phosphoric acid dissolved in 100 c. cs. of water, the third column gives the time delay with 98% sulphuric acid, the fourth column with 25 gms. of acetic acid in 100 c. cs. of water, and the fifth column with 12 gms. of acetic acid in 100 c. cs. of water.

	15/100 phosphoric acid	98% H ₂ SO ₄	25/100 acetic acid	12/100 acetic acid
2° C.....	No initiation in ¾ hour.	No initiation in ¾ hour.	5 min. 2 sec.....	-----
5° C.....	do.....	-----	-----	10¼ min.
10° C.....	do.....	3 min.	2 min. 30 sec.....	6 min.
15° C.....	3 min.	2 min. 30 sec.....	2 min. 30 sec.....	6 min.
20° C.....	2 min. 30 sec.....	40 sec.....	1 min. 30 sec.....	3 min. 17 sec.
25° C.....	3 min. 15 sec.....	30 sec.....	1 min.....	1 min. 5 sec.
30° C.....	2 min. 35 sec.....	20 sec.....	30 sec.....	1 min.
35° C.....	2 min. 55 sec.....	20 sec.....	25 sec.....	1 min. 14 sec.

A further experiment was made using a sodium nitrite-ammonium chloride mixture stabilised with 1½% of magnesium oxide. The initiation was by means of a mixture of acetic and phosphoric acid, buffered with sodium acetate, this having been made up as follows: 125 parts of a solution of 25 gms. of acetic acid in each 100 gms. of water were mixed with 15 parts of sodium acetate. 5 c. c. of this mixture were used.

This was poured on to the sodium nitrite-ammonium chloride mix at various temperatures and the delay times were as shown in the column below.

	Minutes	Seconds
10° C.....	4	40
15° C.....	3	40
20° C.....	2	40
25° C.....	2	20
30° C.....	1	50
35° C.....	1	30

Several practical embodiments of the invention will now be described with reference to the accompanying drawing. Referring generally to the various figures thereof, Figure 1 is a vertical section of apparatus for charging with the liquid

acidic medium. Figure 2 is a vertical section of a somewhat different apparatus for charging with the liquid acidic medium. Figure 3 is a vertical section of a complete blasting assembly, according to my invention, showing the apparatus for charging with liquid acidic medium connected with a charged high tensile steel tube container of the type used for commercial blasting, according to U. S. Patent No. 2,038,772, modified by the omission of the screwed member carrying the terminals, and provided with a venting type of cap rendering stemming or spragging unnecessary.

In Figure 1 a steel body 1 having a portion of reduced diameter 2 is cut with a thread adapted to screw into a corresponding thread in the pressure vessel, not shown, at the end remote from the venting cap and form a substantially gas tight seal. The venting cap is preferably of the type in which the axes of the venting apertures converge rearwardly so that the recoil acts to drive the whole device deeper into the borehole, as described in U. S. Patent No. 2,129,388. The upper part of the body 1 is bored out with a cylindrical cavity of which a portion is cut with a screw to engage a screwed cylindrical portion of a valve member 3 set at its upper portion, at which the screw threads are omitted, in a gland 4, and packing 5, through which the upper part of the valve member 3 is free to be moved to cause its travel up and down the screwed surface of the cavity. At the inner terminal portion the valve member 3 is recessed both in the cylindrical and in the terminal surfaces, and the space bounded by the recess in the said cylindrical sur-

face and the wall of the cavity communicates with a channel 6, bored through from a portion of the wall of the body 1, above the threaded portion of reduced diameter 2. At the entrance to this communicating channel 6, the wall of the body is recessed at 7 to receive the end of a force pump or the like, containing a charge of the liquid to be used. There is also bored through the body 1 a narrow channel 8, from the bottom of the cavity coaxial therewith, so as to emerge in the smaller terminal surface of the body at an orifice 9, of somewhat reduced diameter. The entrance to the channel 8, from the cavity and from the communicating channel 6, is controlled by a soft metal face 10, let into the terminal recess of the valve member 3, this soft metal face closing off the entrance to the channel 8, when the valve member 3, is screwed home. In utilisation the method is to assemble the screwed parts, load the charged cartridge into the borehole with the venting cap inwardly, and the liquid charging apparatus outwardly, inject the liquid through the recess 7 and the orifice 6 while the valve member 3 is in the open position so as to provide a direct channel to the said orifice, whereupon the valve is screwed home so as to seal the channel 8, and the whole device is then ready to effect the blast after the predetermined delay.

In Figure 2 a metal adapter 1 having a portion of reduced diameter 2 is cut with an exterior thread to engage securely the end of a pressure resisting vessel, not shown, of the kind used according to U. S. Patent No. 2,038,772, remote from the venting cap, and to form a substantially gas tight joint therewith. The hollowed out interior of the portion of the adapter 1 of greater diameter is provided with a shoulder and a further cavity beyond the shoulder, both interior cylindrical surfaces being cut with a screw thread, and into the further cavity there is inserted a washer 3 and a piercer 4 which is provided with a channel extending from the cutting point 6 of the piercer to the other end where it communicates with an axial channel 7 in the narrower end of the adapter. The surface leading from the screwed cylindrical surface of the piercer towards its cutting point continues the shoulder of the adapter for a short distance. A washer 8, rests on the shoulder. The other part of this apparatus normally detached from the adapter consists of a small pressure resisting metal container 9 of reduced diameter towards the open end, adapted to contain the liquid acidic medium, the portion of reduced diameter 10 being cut with an external screw thread and adapted to screw into the screwed portion of the adapter 1 to form a substantially gas tight joint. The liquid containing space of the container 9 has a neck of reduced diameter which, however, is opened out to provide two shoulders 11 and 12, and a portion of the inner wall of the broadest section of the neck is cut with a thread. In filling the container the liquid acid medium is run into the container almost up to the inner shoulder, upon which there is placed a pellet 12A of sodium bicarbonate. An oiled disc or paper washer 13 is then laid on the upper shoulder over the pellet and a copper foil diaphragm 14, is placed on top of the washer. A steel washer 15 is placed on the copper foil diaphragm and a threaded steel washer 16 is then screwed home on top of the plain washer. On inverting this upper portion so that the liquid acid medium comes into contact with the sodium bicarbonate pellet a pressure of carbon dioxide is generated and the acidic medium, modified by the presence of the sodium salt of the acid formed, is retained in its place by the copper diaphragm. On screwing the complete upper portion into the adapter 1, the copper diaphragm ultimately comes up against and is pierced by the cutting point 6, so that the acidic medium is forcibly discharged through the channel 7 into the container of the main charge of alkali metal nitrite-ammonium salt mixture. The charged device is placed in the borehole before the copper diaphragm is ruptured.

In Figure 3, 1 represents the apparatus illustrated in Figure 1. This apparatus is screwed into the top of the long steel tube 2 which is of such width as to fit into a borehole. This tube is filled with the sodium nitrite-ammonium chloride mixture 3 and is closed at the lower end by the metal plate 4 which rests on the top of the venting cap 5 which is screwed into the lower end of the tube. The venting cap 5 is provided with venting orifices 6 inclined so that the venting gases force the device further into the bore. The iron plate 4 is adapted to be ruptured when the pressure inside the tube 2 has reached a blasting magnitude. This shows the complete assembly ready to be placed in the borehole when using the apparatus of Figure 1.

The invention is further illustrated by the following examples.

Example 1

The liquid acidic medium consists of a 10% solution of acetic acid; the charge consists of a 380 gm. of a stoichiometric mixture of sodium nitrite and ammonium chloride stabilised by the addition of 2% of its weight of sodium carbonate, granulated in the form of granules passing a 4 and being retained on a 24 B. S. S. mesh sieve. The charge is contained in a steel container of 680 c. c. capacity sealed at one end by a disc adapted to burst at 12 tons per square inch and provided with a venting head of the kind described. The apparatus described in Figure 1 is screwed into position in the container at the remote end from the venting cap. The blasting device is inserted into the borehole with the venting cap towards the closed end. 20 c. cs. of the 10% acetic acid solution are then introduced by means of a small force pump. The valve member is then screwed home. The blast takes place about 2½ minutes after introducing the acetic acid solution when the temperature is about 15° C.

Example 2

The apparatus and blasting charge are as in Example 1. The liquid acidic medium introduced consists of 2 c. cs. of an 18% aqueous solution of chromic anhydride. The blast occurs about 1½ to 2 minutes after its introduction at about 15° C.

Example 3

The charge and container and the venting head are as in the preceding examples, but the apparatus used for the introduction and the liquid acidic medium is that illustrated in Figure 2. The adapter is screwed home into the container. The upper part of the apparatus illustrated in Figure 2 has a capacity up to the inner shoulder of slightly more than 20 c. cs. and 20 c. cs. 45% aqueous phosphoric acid solution are placed in it and a pellet weighing 1½ gms. of sodium bicarbonate is placed on the inner shoulder. The oiled paper washer 13, copper foil diaphragm 14 and the steel washer 15 are then inserted, and the threaded retaining steel washer 16 is then screwed home. This portion of the apparatus is then inverted and left for an hour to allow the sodium bicarbonate time to dissolve. The cartridge is inserted into the borehole with the venting cap towards the back and the portion of its apparatus containing the acid is then screwed home into the adapter. The blast takes place about two minutes after screwing home the upper portion of the apparatus shown in Figure 2 in the adapter at about 12° C.

Example 4

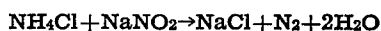
The charge consists of 200 gm. of a stoichiometric mixture of sodium nitrite and ammonium chloride stabilised by the addition of 1½% magnesium oxide, and is in powdery condition. The container for this charge consists of a long high tensile steel tube, closed at one end and open at the other, which is threaded, venting apertures being located near the closed end in the wall of the tube, the axes of the venting apertures are inclined towards the closed end; the materials with which the tube is charged are as follows: nearest to the venting apertures but remotely from the closed end of the tube, a 2" plaster of Paris plug; then immediately up against the plug 6" of sand; and extending from the sand to the open end of the tube a charge of 200 gm. of the

stabilised sodium nitrite-ammonium chloride mixture. The open end of the tube is closed to form a substantially gas tight seal by means of a screw member incorporating non-return means for the introduction of a small volume of a liquid acidic medium into the blasting charge by means of a pressure pipe line from the exterior. The closed blasting device together with the pressure line are stemmed into the borehole with the venting apertures towards the rear, and 5 c. cs. of a 78% aqueous solution of zinc chloride are introduced into contact with the charge from the exterior of the borehole. The blast takes place at about 4 to 5 minutes after the introduction of the zinc chloride solution when the temperature is about 15° C.

I have found that I can obtain excellent results with sodium di-hydrogen phosphate solution, acetic acid in concentration of from 12 gms. to 70 gms. per 100 c. cs. of water, the higher range of from 50 gms. to 70 gms. per 100 c. cs. of water being especially suitable when only a short delay period, i. e. in the neighbourhood of 30 seconds, is required. Ortho-phosphoric acid has a useful range of from 15 gms. to 100 gms. per 100 c. cs., and aluminium sulphate hydrate gives good results at a concentration of 50 gms. per 100 c. cs. Ortho-phosphoric acid and buffered acetic acid having a particularly small temperature coefficient.

Although the invention is based on facts established by experiment an exposition of the theory which I have drawn from these facts will be an assistance to the understanding of the invention, it being understood that the invention is in no way limited by this theory and is not in any way bound up with the correctness or otherwise of the theory.

The equation of the reaction, as given above, in the particular case of ammonium chloride and sodium nitrite is



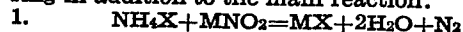
An added acidic medium has no place in this equation and the quantity of this acidic medium would not be altered by the progress of this reaction, but the decomposition of aqueous solutions of ammonium nitrite is known to be accelerated by nitrous acid and by the presence of other not too faintly dissociable acids generally. Even when working with a dry powder the system is not anhydrous, and ammonium nitrite could be formed directly by double decomposition, but the reaction could also be regarded as taking place by the agency of the intermediate formation of nitrous acid from the liquid acid medium and the alkali metal nitrite, and the reaction of the nitrous acid so formed intermediately with the ammonium salt to form nitrogen, an acid and water. In either case the quantity of material converted according to the foregoing equation in a given time must depend upon the available supply of free nitrous acid or hydrogen ions available in the system.

According to the present invention there is suitably introduced into contact with a small portion of the confined solid charge of stable mixture of the alkali metal nitrite and ammonium salt a quantity of liquid acidic medium adapted not only to transform a substantial quantity of the mixture with which it contacts into alkali metal salt, nitrogen and water, but to maintain in contact therewith in the nitrous acid stage of oxidation a substantial fraction of the nitrous acid which may be regarded as being intermedi-

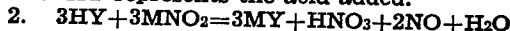
ately generated independently or in the course of that transformation.

The maximum permissible hydrogen ion concentration of the acid medium used is governed by the condition that a substantial fraction of the nitrous acid that may be regarded as independently intermediately generated must be maintained in the oxidation state of nitrous acid. In the case of strong acids with unstabilized mixtures, I have found that the limit corresponds approximately to the hydrogen concentration of a 0.7 normal solution of hydrochloric acid, but already at a normality of 0.5 there is clear evidence of failure to maintain the nitrous acid state of oxidation. Under open conditions this evidence is visible, and consists in the plentiful appearance of brown fumes. I prefer therefore to work at a hydrogen ion concentration lower than that of 0.5 normal HCl.

The gases resulting from the spontaneous decomposition of solid mixtures of sodium nitrite and ammonium chloride contain a little nitric oxide and ammonia; and the increasing amount of brown fume which occurs with dilute strong acid at normalities above about 0.5 to which I have already referred, and the brown fumes produced also when such acid is added to a solution of the solid mixture, are due to one or more side reactions producing nitric oxide, less exothermic than reaction 1 which I may say are much accelerated at low pH. I attribute the failure of the dilute strong acids in part to their greater capacity for diverting the reaction in the direction of the said side reaction or reactions than that possessed by solutions of weak acids and by operative highly concentrated solutions of strong acids such as nitric acid and monochloroacetic acids. The reaction or reactions occurring in addition to the main reaction:



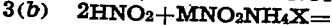
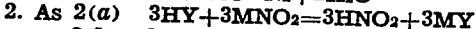
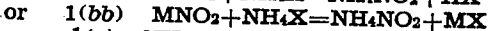
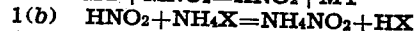
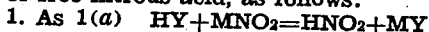
where X represents an acid radical and M an alkali metal, may be written as follows, assuming that HY represents the acid added.



and/or



The reactions 2 and 3 are very much less exothermic than reaction 1, and either of them must result in a diminution of the quantity of acid employed and must leave any unreacted portion of the contacted mixture with excess of ammonium salt over what is required for reaction 1. It is possible however to reformulate all three equations so as to refer the change to the agency of free nitrous acid, as follows:



I consider that the velocity of one or other of the reactions 2(b) or 3(b) is still substantial at the natural pH of a strong acid at a concentration providing no substantial margin over what is required to react with the stabilizer in the solid mixture with which the added volume will contact: and that accordingly the acid will continue to disappear, and that the liquid in contact with the solid mixture passes rapidly through and beyond the pH range which is the most

favourable to the acceleration of the reaction 1. When the strong acid is employed in somewhat higher concentration one or other of these reactions is thus very strongly favoured at the expense of reaction 1; so that, even if the fall in its concentration which occurs as a result of the reaction with the stabiliser and the progress of the said reaction is sufficient to render it no longer highly favourable to their occurrence, too little of the residue of the contacted mixture will be of a composition adapted for the progress of the reaction to provide enough heat to overcome the heat losses in and from the contacted portion. The facts that firstly these reactions are much less exothermic than reaction 1; that secondly they destroy a quantity of one or both of the main constituents of the contacted portion of the mixture, on the extremely high heat evolution of which depends the possibility of a self-propagating decomposition through the mass; that thirdly they load the undestroyed alkali metal nitrite with the cooling effect of a stoichiometric excess of ammonium salt, and fourthly that the presence of acidity besides accelerating the progress of the highly exothermic reaction 1 produces also an acceleration in the side reaction or reactions, to such an extent that if the pH is sufficiently low they overtake the reaction 1, indicate that these side reactions are positively detrimental rather than merely wasteful diversions.

The varied behaviour with stabilised mixtures of both the strong and the weak acids at normalities above about 1, including that of hydrochloric, trichloroacetic, oxalic, acetic, phosphoric, tartaric, and succinic acids is well accounted for by the hypothesis that one or other of these reactions occurs and that at a pH below that of about 0.7 normal hydrochloric acid their velocity is substantial. The hypothesis that for the velocity of reaction 1 to be sufficient for practical purposes it is necessary that the mixture should be maintained in contact with a substantial reservoir of acidic material capable of liberating nitrous acid from salts thereof, but not of rapidly changing its state of oxidation, accounts for the varied behaviour with stabilised and unstabilised mixtures of dilute solutions of strong and weak acids below about 1 normal, and also accounts for the behaviour of strong dibasic acids like sulphuric acid, buffered weak acids, hydrolysable salts of acid reaction, and other solutions capable of being utilised according to the present invention. The acid medium added must accordingly provide at some period in the course of its action on the contacted portion of the charge a substantial reservoir of acid material not of indefinitely high pH, but of a higher and preferably very much higher pH than that of 0.7 normal hydrochloric acid.

Now the conditions obtaining at the contacted portion of a solid charge are much more highly favourable to the velocity of the above termolecular reaction than the conditions obtaining when say a 10 normal solution of hydrochloric acid is added to a bulk of concentrated solution of the mixture. Apart from the absence of the rapid diluting effect on the acid of the water in the solution, the high concentration of the nitrous acid liberated in relation to the water present in the system, the small amount of water available to hold the nitric oxide in solution, and the extension of the nitric oxide solution over a large solid surface exposed to the oxygen of the atmosphere and its consequent removal from the

system as nitrogen peroxide, all may be expected to conduce to the progress of the reaction from left to right at a greater velocity than in a solution of the stabilised mixture.

With regard to the catalysis of the side reaction by acids, this is clearly a hydrogen ion concentration effect. Although the dilution law does not hold at normalities above 0.1 N, the simple strong acids unlike the weak acids show a rapid increase in hydrogen ion concentration as the concentration is increased up to a certain value. If the acid is sufficiently soluble a still further increase may however reduce the hydrogen ion concentration very considerably and in fact reduce it sufficiently to make the acid operative.

By this invention I have revealed a method whereby a blast can be achieved without bringing into the mine any explosive, any combustible material, or any electrical apparatus. The three biggest dangers of blasting in coal mines are therefore obviated, and at the same time the blast can be obtained with certainty, with a delayed action of known time, and with a wide choice as to the length of the delay.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. A blasting cartridge comprising a pressure-resistant container, pressure-rupturable venting means for said container, a charge decomposable in acid media disposed within said container comprising a solid mixture containing alkali metal nitrite and an ammonium salt, means whereby a quantity of acidic medium can be introduced into said container to contact with a portion of said charge, and means for ensuring that said charged container is sealed when decomposition of the charge takes place.

2. A blasting cartridge as claimed in claim 1 in which the means for introducing the acidic medium and the means for ensuring that the charge container is sealed after the introduction of the acidic medium comprise a strong body adapted to close one end of the charge container in a manner sufficiently strong to withstand the pressure in the charge container at all times said body being pierced by a passage adapted to carry the acidic medium from outside the device to the charge and a screw member adapted to close said passage at will in a manner sufficient to withstand the pressure in the charge at all times.

3. A blasting device as claimed in claim 1 in which the means for introducing the acidic medium and the means for ensuring that the container is sealed after the introduction of the acidic medium comprise an acid container adapted to hold the acidic medium, an adaptor sufficiently strong and adapted to close one end of the charge container in a manner sufficient to withstand the pressure in the charge container at all times; said adaptor defining a passage adapted to carry the acidic medium from the acid container to the charge container; a rupturable seal adapted to close the said passage; means for setting up a pressure in the acid container sufficient to force the acidic medium through the said passage when the said seal has been ruptured; and means for rupturing said seal.

4. A blasting cartridge comprising a pressure-resistant container, pressure-rupturable venting means for said container, a charge disposed in said container comprising a solid mixture containing alkali metal nitrite and an ammonium salt, and an initiating medium disposed in initiating relationship with said charge comprising a liquid acidic medium of at least molar normal concentration capable of continuously regenerating hydrogen ions upon reaction with said charge to maintain an alkali nitrite decomposing pH, the hydrogen ion concentration of said liquid acidic medium being less than that of 0.7 normal hydrochloric acid solution.

5. A method of bringing about the initiation of self-sustained decomposition in a confined blasting charge consisting of a solid stabilised alkali metal nitrite-ammonium salt mixture which consists in introducing into contact with a portion thereof a liquid acidic medium of at least molar normal concentration capable of continuously regenerating hydrogen ions as it is consumed to maintain an alkali nitrite decomposing pH, the original hydrogen ion concentration of the acid solution being less than that of a 0.7 normal HCl solution.

6. A method of bringing about the initiation of self-sustained decomposition of a stabilised solid alkali metal nitrite-ammonium salt mixture which consists in introducing into contact with at least a portion thereof a liquid acidic medium of at least molar normal concentration which will maintain in the presence of the alkali metal nitrite and ammonium salt and any other compounds present a pH not greater than 5.2 and not less than 0.25.

7. A method of bringing about the initiation of self-sustained decomposition of a stabilised solid alkali metal nitrite-ammonium salt mixture which consists in introducing into contact with at least a portion thereof a liquid acidic medium of at least molar normal concentration which will maintain in the presence of the alkali metal nitrite and ammonium salt and any other compounds present a pH not greater than 5.2 and not less than 1.0.

8. A method of bringing about the initiation of self-sustained decomposition of a stabilised solid alkali metal nitrite-ammonium salt mixture which consists in introducing into contact with at least a portion thereof a liquid acidic medium of at least molar normal concentration which will maintain in the presence of the alkali metal nitrite and ammonium salt and any other compounds present a pH not greater than 5.2 and not less than 3.5.

9. A method of bringing about the initiation of self-sustained decomposition of a stabilised solid alkali metal nitrite-ammonium salt mixture which consists in introducing into contact with a portion thereof a liquid acidic medium, having a hydrogen ion concentration less than that of 0.7 hydrochloric acid of at least molar normal concentration, comprising an acid of the class which consists of monobasic, dibasic and polybasic acids having at least one dissociation constant lying between 10^{-2} and 10^{-5} at 15°C .

10. A method of bringing about the initiation of self-sustained decomposition of a stabilised solid alkali metal nitrite-ammonium salt mixture which consists in introducing into contact with a portion thereof a liquid acidic medium of at least molar normal concentration comprising an acid of the class which consists of mono-

basic, dibasic, and polybasic acids having at least one dissociation constant of not less than 10^{-5} at 15°C . and which acid is buffered so that it has always a pH of at least 3.5.

11. A method of bringing about the initiation of self-sustained decomposition of a stabilised solid alkali metal nitrite-ammonium salt mixture which consists in introducing into contact with a portion thereof a liquid acidic medium of at least molar normal concentration comprising a salt which in association with the other compounds present yields a pH which lies between 5.2 and 3.5.

12. A method of bringing about the initiation of self-sustained decomposition in a confined blasting charge consisting of a solid stabilised alkali metal nitrite-ammonium salt mixture which consists in introducing into contact with a portion thereof a liquid acidic medium capable of continuously regenerating hydrogen ions as it is consumed to maintain an alkali nitrite decomposing pH said acidic medium being poor in water and consisting of a highly concentrated solution of a highly soluble acid of the class which consists of monobasic and dibasic acids (characterised in dilute solutions as strong acids).

13. A method of bringing about the initiation of self-sustained decomposition in a confined blasting charge consisting of a solid stabilised alkali metal nitrite-ammonium salt mixture which consists in introducing into contact with a portion thereof a highly concentrated acid characterised in dilute solutions as a strong acid but being so poor in water that it has a pH between .25 and 5.2.

14. A method of bringing about the initiation of self-sustained decomposition in a confined blasting charge consisting of a solid stabilised alkali metal nitrite-ammonium salt mixture which consists in introducing into contact with a portion thereof a liquid acidic medium capable of continuously regenerating hydrogen ions as it is consumed to maintain an alkali nitrite decomposing pH which consists of a highly concentrated solution of a highly soluble dibasic acid which, although not necessarily yielding in such concentration a hydrogen ion concentration less than that of a 0.7 normal hydrochloric acid solution, is possessed of a second dissociation constant of weak acid magnitude.

15. A method of bringing about the initiation of self-sustained decomposition in a confined blasting charge consisting of a solid stabilised alkali metal nitrite-ammonium salt mixture which consists in introducing into contact with a portion thereof a liquid acidic medium capable of continuously regenerating hydrogen ions as it is consumed to maintain an alkali nitrite decomposing pH which consists of a highly concentrated solution of a highly soluble dibasic acid which, although not necessarily yielding in such concentration a hydrogen ion concentration less than that of a 0.7 normal hydrochloric acid solution, is possessed of a second dissociation constant lying between 10^{-2} and 10^{-5} .

16. A method of bringing about the initiation of self-sustained decomposition in a confined blasting charge consisting of a solid stabilised alkali metal nitrite-ammonium salt mixture, which method comprises introducing into contact with a portion thereof a soluble, monobasic acid having a dissociation constant not lower than 10^{-5} at 15°C .

17. A method of bringing about the initiation

of self-sustained decomposition in a confined blasting charge consisting of a solid stabilized alkali metal nitrite-ammonium salt mixture, which method comprises introducing into contact with a portion thereof acetic acid in a concentration of not less than 6% in aqueous solution.

18. A method of bringing about the initiation of self-sustained decomposition in a confined blasting charge consisting of a solid stabilized alkali metal nitrite-ammonium salt mixture, which method comprises introducing into contact with a portion thereof orthophosphoric acid in a concentration between 15 and 100 grams per liter.

19. A method of bringing about the initiation of self-sustained decomposition in a confined blasting charge consisting of a solid stabilized alkali metal nitrite-ammonium salt mixture, which method comprises introducing into contact with

a portion thereof a hydrolyzable salt of acid reaction.

20. The method of claim 19, in which the salt is hydrated aluminum sulfate in a proportion of at least 15 grams of hydrated salt to 100 cc. water.

21. The method of claim 19, in which the salt is zinc chloride in a concentration of at least 50 grams per 100 grams water.

22. A method of bringing about the initiation of self-sustained decomposition in a confined blasting charge consisting of a solid stabilized alkali metal nitrite-ammonium salt mixture, which method comprises introducing into contact with a portion thereof an acid salt.

23. The method of claim 22, in which sodium dihydrogen phosphate is the acid salt introduced.

24. The method of claim 22, in which ammonium dihydrogen phosphate is the acid salt introduced.

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