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RESEARCH ON THE SAFETY OF COAL-MINE EXPLOSIVES

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1. Introduction

Coal-mine explosives differ from other general explosives in the following manners: the former does not ignite fire-damp and coal dust in gallery when blasted in fiery mines. The extent of this nature is being termed the "safety" of coal-mine explosives. In order to increase this safety the so-called "inhibitor" is mixed with coal-mine explosives in preventing combustion of methane and coal dust.

Alkali halides are widely being used as the inhibitor for this purpose in all countries of the world. Essentially, the mechanism of ignition of methane by the detonation of explosives is of very complicacy: with general explosives, methane is ignited by the high temperature products of explosion or explosion flame, however, it is observed that with some coal-mine explosives containing abundant inhibitors methane is not always ignited by explosion flame or the explosion products alone. Coal-mine explosive of relatively low detonation velocity belongs to the latter. In regard to the mechanism of ignition of methane, the effect of compression caused by the reflection of shock-wave should he considered.

Numerous experiments have been carried out in the testing gallery with regard to ignition of methane gas under various conditions. The author wishes to report both the results of these experiments referring to the effect of inhibitors, the mechanism of ignition and the theory of safety of coal-mine explosives which are classified as below:

1. Effects of paraffined paper cartridges on safety of explosives
2. Effects of various salts on safety of explosives
3. Variation of safety of explosives when fired from a mortar and exploded in freely suspended state
4. A theory of safety of coal-mine explosives

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2. Effects of paraffined paper cartridges on the safety of explosives

2-1. Method of experiments

The apparatus used in our experiments is a testing gallery, the explosion chamber of which is an iron tube 1.2m. in diameter and 2.7m. long. A mortar with a bore hole 5.5cm. in diameter and 1.20m. long is to be fixed at one end of the gallery. Outline of the testing gallery is illustrated in Fig. 1.

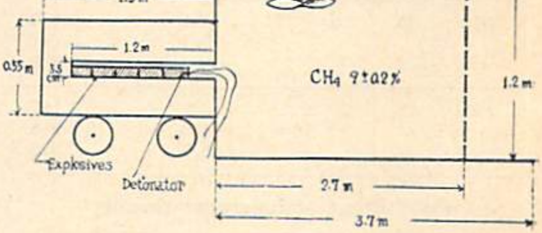

Fig. 1. Outline of a testing gallery

The gaseous mixture in the explosion chamber is made of a mixture of air and 9 ± 0.2 per cent. of methane. The explosive is charged in the bore-hole of a mortar as shown in Fig. 1, and the charge is initiated with a No. 6 electric detonator in the front end of the cartridge nearest the mouth of the bore-hole, and then the explosion of this charge causes ignition of the gaseous mixture in the explosion chamber and its explosion flame is measured by visual observation as to whether all of it has exploded or not.

2-2: Samples and their characteristics

A consideration has been given to the chemical reaction which may occur between the components of the explosive itself and the cartidge case: And several kinds of cartridges has been prepared so that the oxygenbalance of the samples varies in a wide range, for it is assumed that if oxygen is deficient in the composition of explosives, the oxidation reaction of the paper of cartridge cases or paraffine may not occur, but in case of oxygen-riches the excess oxygen may act upon cartridge paper or paraffine. The composition and characteristics of the explosives used are shown in Table 1.

Table. 1. Composition and characteristics of the explosive

No. of Samples	Nitro-glycerine	Nitro-cellulose	Wood Meal	NaCl	NH_4NO_3	Oxygen Balance	Explosion Temperature	Force of Explosives (per 1 kg.)
						g/100g.	°K	kg/cm²-l
No. 1	8.0%	0.3%	0.0%	1.0%	90.7%	+ 18.31	1570	5635
No. 2	8.0	0.3	4.0	1.0	86.7	+ 12.01	1921	6796
No. 3	8.0	0.3	8.0	1.0	82.7	+ 5.71	2270	7910
No. 4	8.0	0.3	12.0	1.0	78.7	− 0.59	2644	9122

All of these samples are powdery explosives. The critical charge weight with which ignition of 9% methane and air mixture would occur or not was sought for, when cartridge cases were unparaffined and paraffined respectively. The critical charge weight above mentioned means the safety limit charge.

2-3. Results of experiments

When unparaffined paper is used as cartridge case, the weight of the case is 2 g to 100 g of explosive, while when paraffined, its weight is about 8 g inclusive of 6 g of paraffine to 100 g of explosive. The results of experiments on safety, using both kinds of cartridge cases are shown in Table 2.

Table 2. Results of experiments on safety to 9% CH_4-air (Maximum non-incendive charge)

No. of samples	Paraffined paper Cartridges	Unparaffined Paper Cartridges
No. 1	50 g	above 400 g
No. 2	40 〃	180 〃
No. 3	60	40 〃
No. 4	100	60

As is obvious in this table, the maximum nonincendive charge differs very much by the cartridges used, i. e. whether the paper of them is made of paraffined paper or not. The illustration of Table 2 is given in Fig. 2.

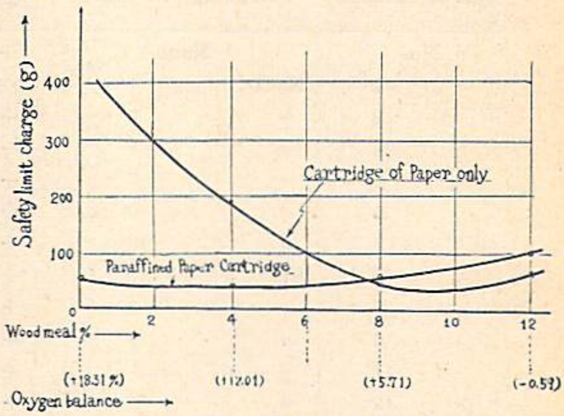

Fig. 2. Effects of paraffined paper cartridges upon safety of explosives of various oxygen balances.

According to the results of these experiments, when there is a large excess of oxygen in composition, the charge with paraffined paper cartridge is very ignitable to methane gas. It is assumed that this is due to the facts that paraffine on a cartridge participates in the chemical reaction in the bore-hole and burns partly and that the temperature of explosion products emerging from the muzzle becomes much higher, whilst that paraffined cartridges, when the composition of explosives is deficient in oxygen, do not cause chemical reactions, rather functioning as inert substances, consequently the safety will be increased.

It has been reported by Taffanel[1] that paraffined paper would reduce the safety of explosives. The explosives used by him were Grisounaphthalite and Grisoudynamite whose oxygen-balances were +13% and +18% respectively, accordingly these were highly oxygen-positive explosives.

The results obtained by Taffanel are to be ascribed to the same chemical reaction as is stated above. Paraffined paper cartridges containing explosives whose oxygen-balances are slightly positive rather increase the safety. Any of ordinary explosives in use in Japan belong to this class and paraffined paper cartridges have proved themselves favourable for the improvement of safety.

3. Effects for various salts on safety of explosives

3–1. Method of experiments

The apparatus and method of experiments are as same as aforementioned.

3–2. Samples of experiments

The explosives used in experiments are mainly composed of such components as 8% nitroglycerine, 0.3% nitrocellulose and 8% wood meal, and the remainder is NH_4NO_3, a portion of which is displaced by salts. The kinds and quantity of salts used are shown in Table 3. (only paraffined paper cartridges are used.)

3–3. Results of experiments on safety

The Table 3 shows the results of experiments on safety of explosives specifically classified into the maximum non-incendive charge and the minimum incendive charge, in relation to the mixture of air with 9 per cent. methane.

Table 3. Effects of various salts on safety of explosives

No. of Samples	Percentage of Salts		Oxygen-Balance (weight %)	Non-incendive Maximum charge	Minimum Incendive charge
No. 1	None		+ 5.71 %	20g.	30g.
2	NaCl	1	+ 5.51	150	200
3	〃	3	+ 5.11	300	350
4	〃	5	+ 4.71	500	550
5	〃	7	+ 4.31	500	550
6	〃	10	+ 3.71	550	600
7	〃	15	+ 2.71	700	750
8	KCl	1	+ 5.51	200	250
9	〃	3	+ 5.11	300	350
10	〃	5	+ 4.71	450	500
11	〃	7	+ 4.31	650	700
12	〃	10	+ 3.71	700	750
13	NH_4Cl	5	+ 2.37	90	100
14	〃	10	− 0.96	100	120
15	Talc	5	+ 4.71	50	60
16	〃	10	+ 3.71	80	100
17	〃	15	+ 2.71	(incomp. expl.)	
18	$NaNO_3$	3	+ 6.52	100	150
19	〃	5	+ 7.06	100	150

20	〃	10	+ 8.42	60	80
21	〃	15	+ 9.78	60	80
22	KNO_3	3	+ 6.30	150	200
23	〃	5	+ 6.69	100	150
24	〃	10	+ 7.67	60	80
25	〃	15	+ 8.65	40	60
26	$CaCl_2$	5	+ 4.71	100	150
27	〃	10	+ 3.71	200	250
28	H_2O	5	+ 4.71	30	40
29	〃	7	+ 4.31	(incomp. expl.)	
30	〃	10	+ 3.71	(no expl.)	
31	Na_2CO_3	5	+ 4.71	200	250
32	K_2CO_3	5	+ 4.71	200	250
33	$(C_4H_4O_6KNa)4H_2O$	5.0	+ 3.57	200	250
34	ICl_3	0.3	+ 5.64	–	100
35	ICl_3 NaCl 3.0, Talc	1.0 3.0	+ 4.24	100	150
36	ICl_3 3.0, NaCl Talc 3.0	3.0	+ 3.84	200	250
37	$Na_2HPO_4 \cdot 12H_2O$	5.0	—	50	60
38	$CH_3COONa \cdot 3H_2O$	5.0	+ 1.77	200	250

The above results are illustrated in Fig. 3.

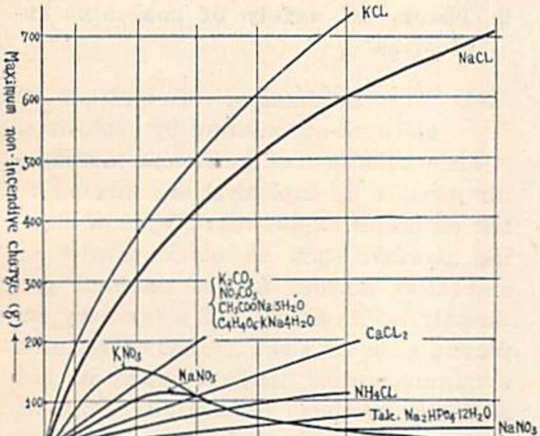

Fig. 3. Safety of explosives containing salts in various proportions. (Firing in the bore-hole of a mortar by direct shot)

It is evident in this experiment that the safety of the explosive charged in the bore-hole of a mortar fixed at one end of the gallery containing the mixture of air and 9 per cent. methane and then fired by means of direct shot differs very much by the kind of the salts to be mixed with the explosive. This suggests that alkali halides, such as KCl or NaCl, are specially effective for prevention of combustion of methane; this proves that the chemical property of added salts is related to the safety of explosives in addition to the effect of reducing the explosion temperature of explosives. Accordingly, the conclusion has been drawn out by the author as follows: a consideration must be given on two factors, i. e. the physical and the chemical effect. The physical effect is such that the effect of salts which control the safety of explosives reduces the temperature or force of explosion, and the chemical effect is such that the salts have the effect of reducing the activity of chain carrier appearing in the chain reaction of methane combustion. Hence, the author is inclined to lay stress upon that any specialist in explosives should be extremely conscientious of these two effects and therefore the author ventures to say that both the view of J. Taylor[2] who emphasises the physical effect and the view of Audibert[3] who stresses the chemical effect are biassed, and it should also be said that the results of Lewis and von Elbe[4]s' research on ignition of methane by such a non-coalmine explosive as tetryl would differ far from the case of coal-mine explosives that contain much inhibitors in them. The author's reports[5] on safety were written in Japanese in details and published in the "Journal of the Industrial Explosives Society, Japan".

4. Variation of safety of explosives when fired from a mortar and exploded in freely suspended state

4-1. Method of experiments

As of the suspension test, experiments have been carried out in such a way that the explosive are suspended freely in the explosion chamber (see Fig. 1), and then exploded to ignite the mixture of air and 9 per cent. methane. Thus the critical charge to ignite methane has been sought for by varying the NaCl content in the sample as in Table 4.

4-2. Results of experiments

The minimum incendive charge and the maximum non-incendive charge to the mixture of air and 9 per cent. methane have been sought for and found as follows.

Table 4. Composition of samples

No.	NG.	NC	Wood meal	NH_4NO_3	NaCl
39	8.0	0.3	8.0	83.7	0
40	〃	〃	〃	82.7	1
41	〃	〃	〃	80.7	3
42	〃	〃	〃	78.7	5
43	〃	〃	〃	76.7	7
44	〃	〃	〃	73.7	10
45	〃	〃	〃	68.7	15

Table 5. Results of suspension explosion test

No.	NaCl %	Detonation velocity (paper cartridge)	Maximum non-incendive charge	Minimum incendive charge
39	0	2390m/s	40g.	50g.
40	1	1930	90	100
41	3	1840	120	140
42	5	1940	90	100
43	7	1980	100	120
44	10	1880	100	120
45	15	1810	100	120

It can be seen in Table 5 that the effect of inhibitors is not notable in the suspension test and the safety limit charge is almost determined by the velocity of detonation. This is the essential point differing from the case in which the safety is greatly increased by increasing the quantity of inhibitors (salts) when fired from a mortar as shown in Fig. 3. Therefore the author draws the following conclusion:—

The safety of explosives to gas is determined by the energy of explosion of the explosive used and the kind of inhibitors contained in it, when fired from a mortar. On the other hand the safety of explosives to gas is mainly determined by the velocity of detonation of the explosive in the suspension exprosion test.

5. Theory of safety of coal-mine explosives

5-1. The mechanism of ignition of methane-air mixture by explosives.

The mechanism of ignition of methane-air mixture by explosives are affected by the nature of explosives; (1) slow burning powder, such as black powder or smokeless powder ignites methane gas directly by its flame, (2) ordinary explosive such as T.N.T., tetryl or common dynamite ignites methane gas by its hot explosion products (essentially same as flame), (3) but coal-mine explosives containing abundant inhibitors ignite methane gas by the collision of reflected shock wave and explosion products.

This conclusion has been obtained after many experiments on the safety of explosives in testing gallery[6]

5-2. A theory of safety of coal-mine explosives

The author formerly made a theoretical consideration[7] about the chemical effect of inhibitors to be mixed with coalmine explosives.

Moreover, the author proposed[8] that it was necessary to consider both the physical effect of reducing the explosion temperature of explosives and the chemical effect of breaking the chain reaction in methane combustion.

The theory however was only descriptive and qualitative, so the author here developes his theory so as to be quantitative or to be of mathematical expression.

The ahthor does not propose any particular mechanism of chain reaction of methane combustion, but he admits some chain mechanism of methane oxidation which is treated by many researchers.[9]

When an explosive in the bore-hole of a mortar fixed at one end of a testing gallery containing CH_4-Air mixture is exploded, chain-carriers in chain reaction of methane oxidation are produced, and chain-branching reaction proceeds with the production of the heat of reaction, accordingly the reaction is accelerated, and it will finally be brought up to thermal explosion.

We denote a quantity of chain carriers produced by the explosion of an explosive as x, and a quantity of inhibitors just sufficient to inhibit the chain reaction as y. Then y should increase according to the quantity of x, but some portion of inhibitor are inefficient because of the collision between inhibitor and non-chain carriers.

So, the change of quantity of inhibitor corresponding to a change of quantity of chain carriers must be

$$\frac{dy}{dx}=\frac{y}{x}\left(1+\beta\frac{y}{x}\right) \qquad (1)$$

where β is some constant.

Now, by denoting a quantity of explosives as w, and a portion of inhibitor to the unit quantity of explosive as p, then the next relations may be obtained.

$$x=kw \qquad (2)$$

$$y=pw \qquad (3)$$

where k is some constant.

If y is assumed to be equal to tx, of which t is a function of x, then the next relation will be obtained.

$$\frac{dy}{dx}=t+x\frac{dt}{dx}$$

Substituting this relation into (1), and after some transformation of this equation, we get

$$x\frac{dt}{dx}=\beta t^2$$

Integrating this equation

$$x=B'e^{-\frac{1}{\beta t}} \qquad (4)$$

where B' is an integral constant.

From (2) and (3), we get

$$t=\frac{y}{x}=\frac{p}{k}$$

and substituting this for (4), the equation becomes

$$x=B'e^{-\frac{k}{\beta p}}$$

Put

$$\frac{k}{\beta}=c$$

then

$$x=B'e^{-\frac{c}{p}} \qquad (5)$$

is obtained and regarding the relation (2), this equation (5) becomes

$$w=Be^{-\frac{c}{p}} \qquad (6)$$

where B is a constant.

The maximum limit charge w for safety is expressed as is in the equation (6) when a consideration is given only on the chemical effect of the action of inhibitor.

Next we must consider the physical effect of inhibitor.

The ignition property of explosives becomes greater as the "force of explosive" is higher. The author assumes that the both variables is inversely proportional. So the safety limit charge w_1 may de expressed as

$$w_1=\frac{A'}{f_0(1-\alpha p)} \qquad (7),$$

where f_0 is "force of explosive" which does not contain any inhbitor, the "force of explosive" f being defined by

$$f=\frac{P_0 V_0 T_0}{273}$$

where $p_0=1.033\text{kg/cm}^2$

V_0=specific volume of explosion products (l/kg)

T_0=temperature of explosion (°K)

and $f=f_0(1-\alpha p)$ where α is the coefficient of reducing "force" calculable by a thermodynamical procedure, and A' is an empirical constant.

Now, the total safety limit charge should be the sum of both physical and chemical limit charges. Therefore, the total limit charge W is obtained from (7) and (6) as below,

$$W=w_1+w=\frac{A'}{f_0(1-\alpha p)}+Be^{-\frac{c}{p}} \qquad (8)$$

With the series of explosives that have various contents of inhibitor and have similar basic compositions, A'/f_0 may remain constant, so the equation (8) may be written as

$$W=\frac{A}{1-\alpha p}+Be^{-\frac{c}{p}} \qquad (9)$$

The equation (8) or (9) is called the equation of safety of coal-mine explosives.

5-3. Determination of constants in the Author's equation of safety of coal-mine explosives

The testing gallery shown in Fig. 1 has also been used for the experiment.

9% CH_4-air mixture is introduced in the explosion chamber and agitated. The explosive is fired with an electric detonator by direct shot.

The samples used are three series of explosives containing NaCl, KCl, and mixtures of NaCl and sea weed as inhibitors. The container for samples is not of paraffined paper, but of ryphan (hydro-chloric rubber) which is not easily combustible and its weight is only 1 g. to 100 g. of sample explosive. The composition is shown in Table. 6.

Table 6. Composition of sample explosives (%)

Series	N G	N G	Wood Meal	Sea Weed	NH_4NO_3+NaCl (KCl)	Remarks
I	8.0	0.3	8.0	—	83.7	NaCl varied
II	〃	〃	〃	—	83.7	K Cl varied
III	〃	〃	4.0	10.0	77.7	NaCl varied

With all these series, fundamental components are remained constant, and NH_4NO_3 and inhibitors (NaCl or KCl) have been changed for the other as in Table. 6

The safety limit charge is determined by observing the explosion and nonexplosion phenomena of geseous mixture. Table 7. shows the results.

Table 7. Safety leimit charge weights (gm)

Inhibitor % \ Series	(I) NaCl series	(II) KCl series	(III) NaCl+10%S.W. series
0	25	25	35
5	285	340	340
10	480	520	605
15	560	630	690
20	585	680	750
25	625	–	–
30	650	–	–

The thermodynamic coefficient of the reducing force of explosive was calculated theoretically as follows,

α=1.24 for NaCl only
α=1.10 for KCl only
α=1.74 for mixed inhibitor of NaCl and 10% sea weed.

Using the data of Table 7 and α, we obtain the constants A, B and C of the safety equation (9), as shown in the Table 8.

Table 8. Constants of equation of safety limit charge

	(I) NaCl series	(II) KCl series	(III) NaCl+10%S.W. series
α	1.24	1.10	1.74
A(g)	25	25	35
B(g)	710	820	970
C	0.050	0.048	0.060

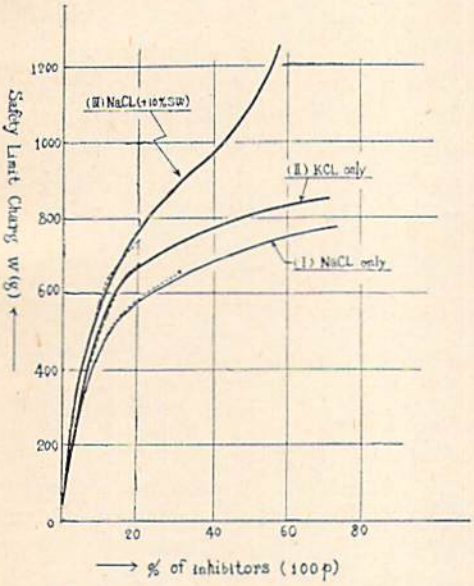

Fig 4. Comparison of experiments and calculations on safety limit charges.

The physical meaning of constants may be that A means the safety limit charge of an explosive which does not contain an inhibitor, B means the highest safety limit charge attainable by the chemical effect alone of inhibitor used, and C means the point of the most acute increase of safety.

5-4. Comparison between experiments and theory

The comparison chart of experimental data and calculated values from the equation (9) is shown in Fig. 4.
In Fig. 4 the full lines show the theoretically calculated values, and the dotted lines show the experimental values.
The agreement of experiments and calculations is satisfactory.

6. Conclusions

1. The effect of paper cartridge for explosives on safety varies largely depending upon the oxygen balance of explosives as shown in Fig. 2. If oxygen is adundant, paraffined paper cartridges reduce the safety, but the un-paraffined does not reduce the safety.

2. Alkali-halides are the most powerful inhibitors to a methane gas explosion. (Fig. 3).

3. In the mortar firing test on safety of explosives, the safety limit charge is determined by two factors, i. e. the explosion energy and the kind of inhibitors contained, but in the suspension explosion test, the safety limit charge is almost determined by the detonation velocity of explosives.

4. The author has proposed a theory on the safety of coal-mine explosives, considering the chain-breaking effect of inhibitors to methane combustion, and it leads to the next equation of safety limit charge weight w, when the explosives contain p parts of an inhibitor.

$$w=\frac{A}{1-\alpha p}+Be^{-\frac{c}{p}}$$

where A=safety limit charge of explosive containing no inhibitor
α=coefficient of reducing " forcc of explosive " of inhibitor contained.
B=maximum safety limit

charge attainable only by the chemical effect of inhibitor contained in explosives

C=most acutely increasing point of safety by any inhibitor contained.

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