RELATIVE HAZARDS OF NITRATES AND CHLORATES

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Relative hazards of nitrates and chlorates
RELATIVE HAZARDS OF NITRATES AND CHLORATES

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The Relative Hazards of Nitrates and Chlorates.

INTRODUCTION.

The hazard of some of the common nitrates and chlorates has been recognized, but encounters with some less well known salts, has brought up the question of their fire hazard. Inquiry then showed that we really had no data on any of the salts by which a comparison of hazards could be drawn. The problem therefore was to devise a set of tests by means of which the relative hazards of the nitrates and chlorates most likely to be encountered in commerce could be judged.

To W.H. Merrill, Manager of The Underwriters Laboratories we are indebted for the use of the equipment of the Laboratories. We are under obligations to Mr. Stewart, for the kind donation of several of the costly salts. To the N.F. P.A. we are indebted for reports on fires chargeable to nitrates and chlorates. With the excellent assistance of Mr. A.H. Nuckolls, Chief Chemical Engineer of The Underwriters Laboratories we were able to make a scientific investigation. With the verified facts and Mr. Nuckolls careful supervision we finally arrived at the conclusions as stated.
GENERAL PLAN OF INVESTIGATION.

The available data that was deemed liable to affect the hazard of the salts was obtained from standard references and from all obtainable records showing fires chargeable to nitrates and chlorates. The salts selected were those used to a wide extent commercially, namely K, Na and Ba, chlorates and K.Na. NH₄, Ba. Sr Th. and Ce. nitrates. Tests were then made to determine the temperature of decomposition, the effects when they were heated pure, the behavior when heated with carbon, when mixed with sulphur, the percentages of moisture in the salts, the rate of burning mixtures of the salts mixed with sawdust, the character of the burning of these mixtures, the temperature of ignition of mixtures, the effect of detonating both the pure salts and mixtures containing combustible matter and the effect of friction on the pure salts and the same mixtures.

EXAMINATION AND TEST RECORD.

Temperature of Decomposition.

Description of Sample.

The pure salts were employed in this test.

Method.

In order to measure the temperatures in this and subsequent tests a thermo-couple was made. To obtain
an electromotive force at the temperatures in this test at which salts decomposed that would be measurable without using a potentiometer, which method consumes considerable time, a couple consisting of "Advance" wire and copper wire was made. The ends of the two wires (both size 24 B & S gauge) were twisted together and welded in an electric arc. They were wrapped together and insulated from each other by asbestos cord, after which all organic material was burned from the cord. The hot junction of the couple was enclosed in a thin quartz tube about \( \frac{1}{2} \) in diameter and 5" long. The other ends were connected to leads which in turn were connected to a suspension galvanometer graduated to read to 0.1 milivolt. The junctions of the leads were wrapped and placed in a tube which was placed in a tube which was packed in ice in order that the cold junction of the couple might at all times remain at 0°C.

The calibration curve of this couple was obtained by plotting galvanometer readings against the boiling points of water and naphthalene and the melting points of cadmium, zinc, and tin. The curve as obtained is shown on the accompanying blue print.

To obtain the electromotive force for the boiling point of water as measured by the thermo-couple
the couple in the tube was placed about \( \frac{1}{4} \) " above 50c.c. of distilled water held in an erlenmeyer flask. The neck of the flask was stuffed with cotton to allow free escape of steam. After boiling the water several minutes a galvanometer reading was taken and recorded. This test was repeated several times on several days and the results were found to check.

The naphthalene was treated in a like manner and the results recorded and plotted.

Pure cadmium was melted in a graphite crucible after having been covered with flake graphite to prevent oxidation, thus forming and impure metal. The couple was inserted in the center of the molten metal, which was allowed to cool very slowly. The readings of galvanometer were taken every minute for the first milivolts change after which they were taken every half minute. The temperature dropped slowly until the freezing point was reached, at which point the galvanometer needle remained stationary for two or three minutes. This test was repeated and the results were found to check. Zinc and tin were treated in a like manner and the results plotted against temperatures.

The salts were placed in an ignition tube and the end of the quartz tube containing the hot junction of the thermocouple was imbedded in the salt. This tube and a delivery tube were led through a stopper made of asbestos fiber and water glass packed in the top of
the ignition tube. The delivery tube was led to a trough and graduated receiving tube so that the gas evolved could be collected over water. The ignition tube was slowly heated in an electric furnace.

Results.

The decomposition of the salts was so very slow even when the temperature was considerable above the decomposition point, that it was judged that this test was of no importance in regard to the hazard of the salts. Furthermore the exact temperature at which the decomposition started was very difficult to ascertain owing to the extreme slowness of the evolution of gas. It was also noted that the salts that had shown themselves to be most hazardous in experience had higher decomposition points then those less hazardous, according to the authorities consulted. Therefore the test was abandoned.

Salts Heated Pure.

Decomposition of Sample.

In these tests the pure salts were used.

Method.

A small quantity of one of the salts was placed in a porcelain crucible and heated with a bunsen burner. The behavior was noted and the gas evolved tested with a glowing splint, to determine the presence or
absence of oxygen. This was repeated for each of the compounds in turn.

**Results**

See plate #1.

**Behavior of Mixtures of Salts and Carbon.**

**Description of Sample.**

Each salt was ground to a powder in a mortar and mixed with carbon black in proportions giving an excess carbon, an excess of salt, and giving the maximum effect in the test.

**Method**

A small quantity of the mixture was placed on a porcelain plate, and ignited (if possible) with a blazing splint. This test was repeated using a glowing splint. Each mixture was then heated with a bunsen flame and the behavior noted. The plate was heated until red hot and small quantities of the various mixtures thrown on it, and the results noted.

**Results**

See plate #1.

**Behavior of Mixtures of Salts and Sulphur.**

**Method.**

This test was identical with the preceding one except that powdered sulphur was substituted for the carbon black.
Amount of Moisture.

Description of Sample.

Pure salts were used.

Method.

Two grams of each salt were accurately weighed on watch-glasses, and placed in an oven and kept at a constant temperature of 98°C. After two hours they were again weighed, replaced in oven and dried until constant weight was obtained. The percent moisture was calculated from the loss in weight.

Rate of Burning.

Description of Sample.

Mixtures consist of 60% powdered salt and 40% sawdust.

Method.

Each mixture was placed in turn in a trough 3/4"X3/4" made of sheet metal. The mixture was then ignited with a red hot wire and the time required to burn 6" along the trough was recorded. The general behavior and the character of the combustion was also noted.

Ignition Temperatures of Mixtures.

Description of Sample.

Mixtures consisting of 60% salt and 40% sawdust were used in this test.
Method

An electric furnace (resistance type) was heated to 350 °C. The temperature was measured with the thermo-couple as described in the first test. The quartz tube was removed while obtaining these results. Each end of the tube of the furnace was closed with a sheet of mica, the couple projecting through a slit in the one in the front. After the temperature of the furnace had reached the desired value, the current was adjusted by a rheostat so that the furnace would remain at that temperature. Moving the couple to different positions in the furnace showed that when once a constant value was reached the temperature throughout the middle half of the furnace was the same. With the temperature at the desired value a porcelain boat with some of the salt-sawdust mixture in it was placed in the furnace. The time required for the mixture to ignite and burn was noted, that is if the mixture did ignite. Tests on each salt were run with the furnace at 100-150, -200, -250, -300, -350°C. The lowest temperature at which each mixture would ignite was recorded. This method gives the ignition point within 50°C. It was not considered necessary to obtain closer results.
Detonation

Description of Sample.

The salts in the pure state and mixtures of the salts with carbon and sulphur were subjected to this test.

Method

The samples were struck with a steel hammer when lying on a clean steel plate, on a cement floor and on a wooden board.

Friction

Description of Sample

The same samples used in the preceding test were subjected to this test.

Method

The samples were rubbed with steel on steel, cement, and wood. The rubbing was done by hand with the cleaned face of a hammer.

Effect of Water on Fires.

Description of Sample

Mixtures consisting of 60% salt and 40% sawdust were employed.

Method

A few ounces of each sample were placed on an iron dish and ignited. When the fire had gained full headway a fine stream of water from a wash bottle was thrown on it. In every case the fire was
Method. (Concl.)

extinguished without any difficulty showing that the effect of water on nitrate and chlorate fires is the same as on any other hot fire, showing that the notion that water caused explosions was not based on fact.
INTERPRETATION OF RESULTS.

The results of the tests described above have been compiled and united into a single table, which is shown on an accompanying blue print. (Plate I). From these results the salts have been arranged in the order of their hazards as shown by each particular test. These tables of arrangement were then combined into a single table with a column for each test, and from this table, with the general behavior of the compounds in mind, the final conclusions have been drawn.

Key:    "A" - Barium chlorate - Ba(ClO₃)₂
         "B" - Sodium chlorate - NaClO₃
         "C" - Potassium chlorate - KClO₃
         "D" - Potassium nitrate - KNO₃
         "E" - Sodium nitrate - NaNO₃
         "F" - Ammonium nitrate - NH₄NO₃
         "G" - Strontium nitrate - Sr(NO₃)₂
         "H" - Barium nitrate - Ba(NO₃)₂
         "I" - Cerium nitrate - Ce(NO₃)₄
         "J" - Thorium nitrate - Th(NO₃)₄

Note: A brace { indicates that all included fall in a group and that no distinction can be made between the members of the group.

A bracket [ indicates a group but the members of it can be distinguished in the order named.
Test #1.

(Heating of pure salts,--product and behavior when tested with a splint.)

F This compound is given first place in hazards as shown by this test because the salt bursts into flame when heated.

These three grouped and given second place because they all evolve oxygen and give a flash when treated with a splint.

Given next place because they cause rapid burning of the splint and evolve oxygen.

Both H and G give rapid burning of the splint at red heat. H is ranked first as it seems to give this result at a lower temperature than G.

Grouped because both give off brown fumes which support combustion but do not give very rapid burning. I is placed ahead of J because a glowing splint is extinguished in J but not in I.

Test #2.

(Mixtures of salts with carbon black)

These three are grouped because all ignite from a burning splint and give a flash. A is given first place because the flash was obtained over a wider range of mixtures than with the other two. C is ranked second because all mixtures light from a
blazing splint, whereas one with B did not. B gave rapid burning only when an excess of salt was present. This mixture would not ignite from a splint.

D Mixtures did not flash but gave fast burning when a splint was applied. All mixtures ignited from a blazing splint.

E The burning was slower than with D, but otherwise behaved about the same. The mixture containing an excess of salt would not ignite from a splint.

F The burning was still slower and the mixtures ignited from a splint.

I Mixtures ignited from a splint except where an excess of salt was present. The burning was slow.

G The mixtures of these two salts would not ignite from a splint. When heated the carbon burned out before the salts decomposed. When thrown on a red hot crucible lid they burned with bright flames. They are placed after I because they would not ignite.

J Placed last because mixtures would not ignite from splints and when thrown on hot lid the salt decomposed and some of the carbon burned, but there was no flame.

Test #3.

9 (Mixtures with sulphur.)

A These three gave a flash with a splint and when heated, and are therefore placed first.
D Gave a slow flash.
E Gave slower burning.
F The sulphur burned and the salt vaporized when the mixture was treated with a splint and when it was heated. A brilliant flash was obtained when the mixture was thrown on a hot lid.
G The sulphur burned out as above but a flame was obtained instead of a flash on the hot lid. Hence G is placed below F. H gave results about the same as were obtained with G except that the burning seemed to be a little slower and less intense.
J A glowing splint was extinguished. The mixtures blazed a trifle on the hot lid.
I Gave no blaze. The sulphur burned in air.

Test #4.
(Percentage moisture.)
A,B,C,D,E,F,G,&H. Grouped together since all have less than .2% moisture.
J 4.34%.
I 17.33%.

Test #5.
(Average time it takes mixtures of 60% salt and
40% sawdust to burn 1 inch in a trough 3/4" x 3/4".

D 7.5 seconds.
A 11 "
B 15 "
F 16 "
C 17 "
E 30 "
I 200 "

Mixtures with these three salts would not continue to burn when once ignited.

Test #6.
(Characteristic of burning of mixtures used in #5.)

These three salts gave brilliant flames.

The flames were less intense than with the above mixtures.

F Gave rapid smouldering.
I Gave slow smouldering.

Would not burn.

Test #7.
(Ignition points of the same mixtures).

I 100-150 degrees centigrade.
F 150-200 " " 
B 200-250 degrees centigrade.

ACDEJ 250-300 " "

GH Above the ignition point of wood.

Test #8.
(Detonation.)

ACE These three chlorates were detonated pure and when mixed with combustibles. No difference in the ease of detonation could be noted.

D The remainder of the salts could not be detonated.

Test #9.
(Friction.)

AB Both of these salts gave explosions on steel and on cement when mixed with combustibles, and gave cracking on wood. When pure they gave cracking when rubbed with steel on steel and with steel on concrete.

C Behaved the same as the above two except that the cracking on wood could not be obtained. Hence it is rated lower.

D The remainder of the salts could not be affected by friction.
Table combining all of above results.

<table>
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<tr>
<th>Test No.</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>#5</th>
<th>#6</th>
<th>#7</th>
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<td>I</td>
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<td>J</td>
<td>J</td>
<td>H</td>
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</table>

CONCLUSIONS

From the above data and a consideration of the relative importance of the tests from which the data has been obtained, the salts may be divided into groups as follows:

**Group I.**

A, B, and C, the chlorates, deserve to be rated in a class by themselves since they not only give the most intense burning and rapid flashes, but they also have an ignition hazard that the nitrates do not have, since both when pure and when mixed with combustibles they can be ignited and exploded by detonation and friction.

**Group II.**

D, E, and F. These three nitrates comprise a second
class because there is a wide difference between their manner of burning and that of the chlorates above and that of the nitrates below. F has a slower rate of burning than D and E but the ignition point is quite low and the pure salt burns, so it is judged that it should come in this class. Its rate of burning is very much greater than that of the salts in the class below. The conduct of D is very similar to that of E in all the tests.

Group III.

G, H, I, and J. Mixtures of these nitrates with sawdust will not burn when ignited, except I, which smoulders very slowly. The behavior of all these salts when mixed with combustibles as noted in tests #2 and #3 is decidedly different from that of the members of group II, since none in group III will ignite from a splint.

Carrying the classification still further we can make a distinction among the members of each group and arrange them according to their fire hazard.

Group I.

1st. A. This compound is ranked first in this group since it shows hazards greater than B and C in tests #2 and 3, greater than C in #9, and the same as B and G in #1, 3, 4, 6, and 8. Together with C it falls under
B in #7 but here the ignition points fall in the next 50 degrees so that this difference in hazard is not great.

2nd. B. B falls above C in #5, 7, and 9, all of which are important tests. They easily overbalance the slightly lower position in #2. In all other tests it ranks even with C.

3rd. C. Last of group.

Group II.

1st. F. This salt is ranked first in hazard in its group on account of the low ignition point and because of the fact that the pure salt will burn. These facts are deemed to overbalance the slightly lower position of this compound in #2, 3, and 6. It falls between D and E in #5 and even with them in #4.

2nd. D. D is placed above E on account of its higher rank in tests #2, 3, and 7. It does not fall below E anywhere but ranks even with it in #1, 4, 6, and 7.

3rd. E. Last of group.

Group III.

1st. I. I is given first place on account of the very low ignition point and the fact that the mixture with sawdust will smoulder, whereas other mixtures of this group will not burn. These facts are indicated by the rank of I above G, H, and J in #5, 6, and 7. These differences have been considered more important.
than the low position in #1, 2, 3, and 4, as the differences between I and the rest of the group are more marked.

2nd. and 3rd. G and H. These two must be rated together as no appreciable difference in behavior was noted in any test. They are ranked above J because their mixtures with combustibles will burn when heated, while no flame can be obtained with J. They appear above J in every test except in #7 and there J shows a pretty high temperature of ignition itself.

4th. J. Last of group.

**SUMMARY.** -- Final Table.

Groups and individual salts in the order of Hazard.

**Group I.**

A - - Ba(ClO₃)₂
B - - NaClO₃
C - - KClO₃

**Group II.**

F - - NH₄NO₃
D - - KN₂O₃
E - - NaNO₃

**Group III.**

I - - Ce(NO₃)₄
G - - Ba(NO₃)₂
H - - Sr(NO₃)₂
J - - Th(NO₃)₄

*Within groups:*

I. Difference not pronounced; hardly appreciable.

II. Difference fairly well defined.

III. Difference appreciable.

Difference between groups is quite pronounced.
<table>
<thead>
<tr>
<th>TEST</th>
<th>PURE SALT HEATED</th>
<th>MIXTURES CARBON:BLACK+SALT</th>
<th>MIXTURES SULPHUR+SALT</th>
<th>MOISTURE RATE OF BURNING</th>
<th>IGNITION POINT °C</th>
<th>DETONATION</th>
<th>FRICTION</th>
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<tbody>
<tr>
<td>SALT</td>
<td>CLOWING SPINT INSERTED</td>
<td>EXCESS CARBON BURNS SLOWLY</td>
<td>SPLINT GIVES GREEN FLASH</td>
<td>0.06%</td>
<td>250°-300°</td>
<td>PURE EXPLOSION</td>
<td>STEEL ON STAINLESS STEEL, CRACKING EXPLOSION</td>
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<td>Ba(NO₃)₆</td>
<td>MELTS BUBBLES OFF OXYGEN</td>
<td>SPINT BURNS WITH FLASH</td>
<td>SPINT GIVES GREEN FLASH</td>
<td>0.05%</td>
<td>15 SECONDS</td>
<td>INTENSE FLAME</td>
<td>STEEL ON STEEL, CRACKING</td>
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<td>SPLINT BURNS</td>
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<td>DECOMPOSES AT RED HEAT OF CRYSTAL</td>
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<td>WILL NOT BURN</td>
<td>IGNITION POINT OF WOODE</td>
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