Stabilizing Firework Compositions
I. Minimum Solubility Law to Foresee the Degeneration
II. A New Chemical Method of Magnesium Coating

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ABSTRACT

These studies concern two important problems at present: one is how to select the component materials of a mixture not to cause degeneration, and another is to find a more effective method of magnesium coating than those at present.

A firework mixture generally consists of several solid materials which are closely in contact with each other. The state is not so much natural as artificial. Therefore, the mixture often causes chemical degeneration to remove into a more stable state which is opposite to the purpose. The direction of the change has been unknown without experiences. It has been a great difficulty on selecting materials. I have found a rule to foresee the direction: the component materials in a mixture gradually decompose with each other to create the most water insoluble material. This tendency should be called the "minimum solubility law". A table was prepared to foresee the direction of the degeneration reactions arranging materials in the order of their solubilities.

When a magnesium flake is soaked in a solution of dichromate and sulfate, the flake is gradually coated with a thin black film. It may be CrO_2 and have a high corrosion resistance. The effect was tested with several dichromates and sulfates against mainly ammonium perchlorate using magnesium ribbon and powder. In addition an effect of guanidine nitrate on the coating was observed because it gave a good result of corrosion resistance when it was used as a blinker (strobes) in the past.

1. Introduction

A firework composition generally consists of several materials, oxidizer, fuel, color producing agent, etc. The state of the mixture is not natural, but artificial. The materials are closely in contact with each other. Therefore, the mixture very often gradually degenerates chemically or sometimes physically to a more stable state. It causes many troubles, moisture absorption, no ignition, low light intensity, spontaneous ignition, etc.

The most important problems at present in the firework field to avoid the degeneration of mixture may be how to select the materials and how to protect metal powders especially magnesium from corrosion.

With the former we could have no reliable evidence without experiences in the past. However, with individual experience we cannot foresee the general rule. For example, R. Lancaster wrote "Never mix chlorates with ammonium salts".[1] On the other hand, in the German regulation we find that a mixture of chlorate and ammonium salt is forbidden, however, that of chlorate and ammonium chloride is allowed.[2] Another example is that: nitrate with ammonium salt is generally avoided due to producing a hygroscopic substance, but barium nitrate with ammonium perchlorate can be used with no hygroscopic troubles.[3] This paper will solve such contradictions and give us a general rule on the selection of the materials.

With the latter, many methods of physical or chemical coating are already presented.[4] However, it has been difficult to find the method to

protect magnesium from corrosion intensive ammonium perchlorate which is important to make blinkers (strobes).

This paper suggests a new chemical coating method which may be more useful than those at present.

2. The Minimum Solubility Law

2.1 General Principles and Applications

The chemistry originally developed from a dilute solution of some substances in water or from vapor phase. However, our firework mixtures are in solid phase. The degeneration reaction occurs from a solid to solid among the component materials. From our experiences in almost all cases, we know the degeneration of such mixtures occurs from absorption of moisture in the air. Therefore, the state of our mixtures should be thought to be a highly concentrated solution of materials in water, where only the minimum amount of moveable ions of the materials will exist.

A traditional example of producing a precipitate in a dilute solution at 30 °C is shown with the reaction of silver nitrate with sodium chloride:

$$AgNO_3 \; + \; NaCl \; \rightarrow \; AgCl\downarrow \; + \; NaNO_3$$

$$216 \qquad 36.1 \qquad 0.00024 \qquad 96.0$$
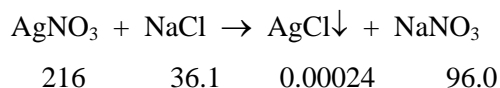
where the figures under symbols show the solubility of each material in 100 grams of water at 30 °C, the horizontal arrow shows the direction of proceeding of the reaction, and the downward arrow shows the formation of precipitate. These expressions are used hereafter. When the data of solubility of individual substance are not available at 30 °C, those of near 30 °C are used.

As it is seen in above formula, the reaction proceeds from the left side to the right. In a dilute solution of materials, it is a very common rule of a double decomposition (i.e., the reaction in a dilute solution proceeds to form a substance which has the minimum solubility of all). The firework mixtures, especially when they are consolidated, are not a dilute solution, but a solid. However, as described above, they may be thought to be a highly concentrated solution in water because they absorb more or less a very small amount of moisture. Therefore, even in the consolidated state the reaction may proceeds in the direction to produce a substance of minimum solubility as it is with the precipitate formation in the dilute solution. However, it takes a long time, several days, months or years because of few active ions. In this paper the author calls this reaction rule as the "minimum solubility law".

A table was prepared to confirm above theory or to foresee the directions of degeneration reactions (Table 1). In the table, materials are arranged in the order of their solubilities.

A few examples of foreseeing the degeneration reactions are presented from Table 1.

Notes for Table 1:

a) The arrangement in Table 1 is as follows:

Material																			
			Order Number of Solubility																
Material	Solubility in 100 g of Water	Order Number of Solubility	−	e	e	e	e	e	e	e	e	e	e	e	e	e	Order number of Solubility	Nateruak
			e	−	e	e	e	e	e	e	e	e	e	e	e	e		
			e	e	−	e	e	e	e	e	e	e	e	e	e	e		
			Direction of Degeneration (Stability)																
			e	e	e								e	e	e		
			e	e	e	e	e	e	e	e	e	e	e	e	e	e		
			e	e	e	e	e	e	e	e	e	e	e	e	e	e		
			e	e	e	e	e	e	e	e	e	e	−	e	e		
			e	e	e	e	e	e	e	e	e	e	e	−	e		
			e	e	e	e	e	e	e	e	e	e	e	e	−		

b) Symbols for materials are denoted in combination of cation with anion:

Cation 1: K−   Anion: A: −NO$_3$ H: =Cr$_2$O$_7$
        2: Na−   B: −ClO$_3$ I: −Cl
        3: Sr=   C: −ClO$_4$ J: =C$_2$O$_4$
        4: Ba=   D: =CO$_3$
        5: Ca=   F: =SO$_4$
        6: NH$_4$−   G: =CrO$_4$

For example, potassium nitrate is denoted by 1A which means KNO$_3$ or Strontium carbonate by 3D which means SrCO$_3$.

c) General symbols:

   S: no reaction, stable,
   s: stable due to common ions between two materials,
   x: degenerates, unstable
   a: unstable when alkaline,
   ?:   uncertain due to no data of solubility,
   *:   no data when acid is formed, but certain with experiment.

d) The data of solubility were taken from reference 5. These are the values at or near 30 ℃.

The reaction of potassium chlorate (1B) and ammonium perchlorate (6C) is found at the crossing point of the horizontal line of 1B with the vertical line of 6C as a symbol x which denotes unstable. This reaction is expressed as:

$$KClO_3 + NH_4ClO_4 \rightarrow$$
$$\quad 10.1 \qquad 29.9$$
$$\qquad\qquad KClO_4\downarrow + NH_4ClO_3 \qquad (1)$$
$$\qquad\qquad 2.6 \qquad\qquad 53.4$$
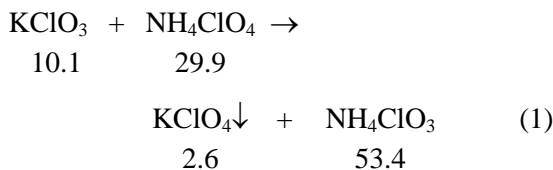
In the same way with potassium chlorate (1B) and ammonium chloride (6I) the crossing point denotes stable with a symbol S:

$$KClO_3\downarrow + NH_4Cl \leftarrow$$
$$\quad 10.1 \qquad\quad 41.4$$
$$\qquad\qquad KCl + NH_4ClO_3 \qquad (2)$$
$$\qquad\qquad 37.2 \qquad\quad 53.4$$

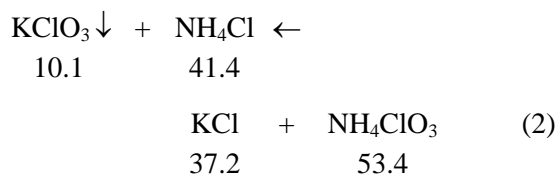**Table 1. Table for Foreseeing Degeneration Reaction at 30 ºC with Two Materials in a Solid Mixture Based on the Minimum Solubility Law.**
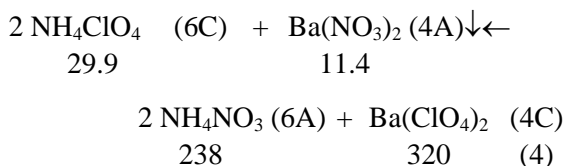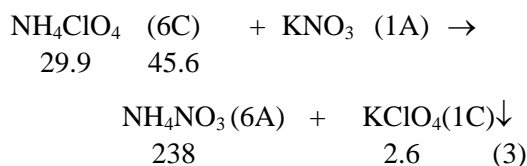
			4F	4G	5J	3D	3F	4D	3J	4J	5D	3G	5F	1C	2J	1B	4A	1F	5G	1H	6C	2I	1I	4I	6G	1J
		No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
4F	0.00029	1	–	s	S	S	s	s	S	s	S	S	s	S	S	S	s	s	S	S*	S	S	S	s	S	S
4G	0.00046	2	s	–	S	S	x	s	S	s	S	s	x	S	x	S	s	x	s	S*	S	S	S	s	s	S
5J	0.00073	3	S	S	–	S	S	S	s	s	s	S	s	S	s	S	S	S	s	S	S	S	S	S	S	s
3D	0.00090	4	S	S	S	–	s	s	s	S	s	s	S	S	S	S	S	S	S	S	S	S	S	S	S	S
3F	0.00138	5	s	x	S	s	–	x	s	S	x	s	S	S	S	S	x	s	S	S	S	S	S	x	S	S
4D	0.0034	6	s	s	s	s	x	–	x	s	s	x	x	S	S	S	s	x	x	x	S	S	S	s	S	S
3J	0.00461	7	S	S	s	s	s	s	–	s	x	s	x	S	s	S	S	x	x	?	S	S	S	S	S	s
4J	0.0140	8	s	s	s	S	S	s	s	–	x	x	x	S	s	S	S	x	x	?	S	S	S	s	x	s
5D	0.072	9	S	S	s	s	x	s	x	x	–	x	s	S	x	S	x	S	s	S	S	S	S	x	S	x
3G	0.096	10	S	s	S	s	s	x	s	x	x	–	x	S	x	S	x	x	s	?	S	S	S	x	x	x
5F	0.209	11	s	x	x	S	S	S	x	x	s	x	–	S	x	S	x	s	s	S	S	S	S	x	S	x
1C	2.6	12	S	S	S	S	S	S	S	S	S	S	S	–	S	s	S	s	S	s	s	S	s	S	S	s
2J	3.8	13	S	x	s	S	S	S	s	s	x	x	x	S	–	S	x	S	x	S	S	s	S	x	S	x
1B	10.1	14	S	S	S	S	S	S	S	S	S	S	S	s	S	–	S	s	S	s	x	S	s	S	S	s
4A	11.4	15	s	s	S	S	x	s	S	s	x	x	x	S	x	S	–	x	x	x	S	S	S	s	x	x
1F	13.0	16	s	x	S	S	s	x	x	x	S	x	s	S	S	s	x	–	x	s	x	S	s	x	S	s
5G	16.1	17	S	s	s	S	S	x	x	x	s	s	s	S	x	S	x	x	–	S	S	S	S	x	s	x
1H	19.1	18	S*	S*	S	S	S	x	?	?	S	?	S	s	S	s	x	s	S	–	S	S	s	?	S	s
6C	29.9	19	S	S	S	S	S	S	S	S	S	S	S	s	S	x	S	x	S	x	–	S	x	S	s	x
2I	36.1	20	S	S	S	S	S	S	S	S	S	S	S	S	s	S	S	S	S	S	S	–	s	s	S	x
1I	37.1	21	S	S	S	S	S	S	S	S	S	S	S	s	S	s	S	s	S	s	x	s	–	s	S	s
4I	38.3	22	s	s	S	S	x	s	S	s	x	x	x	S	x	S	s	x	x	?	S	s	s	–	x	x
6G	39.9	23	S	s	S	S	S	S	S	x	S	s	S	S	S	S	x	S	s	S	s	S	S	x	–	S
1J	40.1	24	S	S	s	S	S	S	s	s	x	x	x	s	s	s	x	s	x	s	x	x	s	x	S	–
2F	41.2	25	s	x	S	S	S	S	x	x	S	x	x	S	x	S	x	s	x	x	S	s	x	x	S	x
6I	41.4	26	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	s	s	s	s	s	s
4B	41.7	27	s	s	S	S	x	s	S	s	x	x	x	S	x	s	s	x	x	?	S	S	x	x	x	x
2D	45.3	28	S	S	S	s	x	s	x	S	s	x	x	S	s	S	x	S	x	S	S	s	x	x	S	x
1A	45.6	29	S	S	S	S	S	S	S	S	S	S	S	s	s	S	s	s	S	s	x	S	s	x	S	s
6H	46.5	30	?	?	S	?	?	?	?	?	S	?	S	S	S	S	?	S	S	s	s	S	x	?	s	x
6B	53.4	31	S	S	S	S	S	S	S	S	S	S	x	S	S	s	S	x	S	x	s	S	x	x	s	x
6D	55.8	32	S	S	S	s	x	s	x	x	s	x	x	S	x	S	x	S	x	S	s	S	S	x	s	S
3I	58.5	33	S	S	S	s	s	x	s	x	x	s	x	S	x	S	x	x	x	?	S	s	s	x	x	x
6J	59.0	34	S	S	S	S	S	S	s	s	x	x	x	S	s	S	x	S	x	S	s	x	S	x	s	s
1G	66.1	35	S	s	S	S	S	S	S	x	S	s	S	S	s	S	x	s	s	s	S	S	S	s	s	s
6F	77.8	36	s	x	S	S	s	x	x	x	S	x	s	S	S	S	x	s	x	x	s	S	x	x	s	x
5H	83.0	37	?	?	s	?	?	?	?	?	s	?	s	S	x	S	?	x	s	s	S	S	x	?	x	x
2G	88.0	38	S	s	S	S	S	x	S	x	S	s	S	S	s	S	x	S	S	S	S	s	x	x	s	x
3A	88.7	39	S	S	S	s	s	x	s	x	x	s	x	S	x	S	s	x	x	ax	S	S	S	x	x	x
2A	96.0	40	S	S	S	S	S	x	S	S	S	S	S	S	s	S	S	x	S	S	S	s	x	x	S	x
5I	100	41	S	S	S	S	S	S	x	x	s	S	s	S	x	S	S	x	s	S	S	s	s	s	S	x
2B	105	42	S	S	S	S	S	S	S	S	S	S	S	S	s	s	S	x	S	x	S	s	x	x	S	x
1D	114	43	S	S	S	s	x	s	x	x	s	x	x	S	S	s	x	s	x	s	x	S	s	x	S	x
5A	153	44	S	S	S	S	S	S	x	x	s	S	s	S	x	S	s	x	s	S	S	S	S	x	x	x
3B	178	45	S	S	S	s	s	s	s	x	x	s	x	S	x	s	s	x	x	?	S	S	x	S	x	x
2H	192	46	?	?	S	?	?	?	?	?	S	?	S	S	s	S	?	S	S	s	S	s	x	?	S	x
5B	194	47	S	S	S	S	S	S	x	x	s	S	s	S	x	s	S	x	s	x	S	S	x	S	x	x
5C	202	48	S	S	S	S	S	S	x	x	s	S	s	s	x	x	S	x	s	x	s	S	x	S	x	x
2C	219	49	S	S	S	S	S	S	S	S	S	S	S	s	S	x	S	x	S	x	s	s	x	x	x	x
6A	238	50	S	S	S	S	S	S	S	S	S	S	S	S	S	S	s	S	S	S	s	S	S	x	s	S
4C	320	51	s	s	S	S	x	s	S	s	x	x	x	s	x	x	s	x	x	?	s	S	x	s	x	x
3C	327	52	S	S	S	s	s	x	s	S	x	s	x	s	x	x	S	x	x	?	s	S	x	S	x	x

Table 1. Table for Foreseeing Degeneration Reaction at 30 ºC with Two Materials in a Solid Mixture Based on the Minimum Solubility Law. (Continued)

| 2F | 6I | 4B | 2D | 1A | 6H | 6B | 6D | 3I | 6J | 1G | 6F | 5H | 2G | 3A | 2A | 5I | 2B | 1D | 5A | 3B | 2H | 5B | 5C | 2C | 6A | 4C | 3C | | |
25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	52	52	No.	4F
s	S	s	S	S	?	S	S	S	S	S	s	?	S	S	S	S	S	S	S	S	?	S	S	S	S	s	S	1	4F
x	S	s	S	S	?	S	S	S	S	s	x	?	s	S	S	S	S	S	S	S	?	S	S	S	S	s	S	2	4G
S	S	S	S	S	S	S	S	S	s	S	S	s	S	S	S	s	s	S	s	S	S	s	s	S	S	S	S	3	5J
S	S	S	s	S	?	S	s	s	S	S	S	?	S	s	S	S	S	s	S	s	?	S	S	S	S	S	s	4	3D
s	S	x	x	S	?	S	x	s	S	S	s	?	S	s	S	S	S	x	S	s	?	S	S	S	S	x	s	5	3F
x	S	s	s	S	?	S	s	x	S	x	x	?	x	x	x	S	S	s	S	x	?	S	S	S	S	s	x	6	4D
x	S	S	x	S	?	S	x	S	s	S	x	?	S	s	S	x	S	x	x	S	?	x	x	S	S	S	s	7	3J
x	S	s	x	S	?	S	x	x	s	x	x	?	x	x	S	x	S	x	x	x	?	x	x	S	S	s	S	8	4J
S	S	x	s	S	S	S	s	x	x	S	S	s	S	x	S	s	s	s	s	x	S	s	s	S	S	x	x	9	5D
x	S	x	x	S	?	S	x	x	x	x	x	?	s	s	S	x	S	x	S	x	?	S	S	S	S	x	s	10	3G
s	S	x	x	S	S	x	x	x	x	S	s	s	s	s	S	x	x	x	x	x	S	s	s	S	S	x	x	11	5F
S	S	S	S	s	S	S	S	S	S	s	S	S	S	S	S	S	S	s	s	S	S	S	s	s	S	s	s	12	1C
s	S	x	s	S	S	S	x	x	s	S	S	x	S	x	S	x	s	S	x	x	s	x	x	s	S	x	x	13	2J
S	S	s	S	s	S	s	S	S	S	s	s	S	S	S	S	S	s	s	S	s	S	s	x	x	S	x	x	14	1B
x	S	s	x	s	?	S	x	S	x	x	x	?	x	s	s	S	S	x	s	S	?	S	S	S	s	s	S	15	4A
s	S	x	S	s	S	x	S	x	S	s	s	x	S	x	x	x	x	s	x	x	S	x	x	x	S	x	x	16	1F
x	S	x	x	S	S	S	x	x	x	x	x	s	s	x	S	s	S	x	s	x	S	s	s	S	S	x	x	17	5G
x	S	?	S	s	s	x	S	?	S	s	x	s	S	ax	S	S	x	s	S	?	s	x	x	x	S	?	?	18	1H
S	s	S	S	x	s	s	s	S	s	S	S	S	S	S	S	S	S	x	S	S	S	S	s	s	s	s	s	19	6C
s	s	S	s	S	S	S	S	s	x	S	S	S	s	S	s	s	s	S	S	S	s	S	S	s	S	S	S	20	2I
x	s	x	x	s	x	x	S	s	S	s	x	x	x	S	x	s	x	s	S	x	x	x	x	x	S	x	x	21	1I
x	s	s	x	x	?	x	x	s	x	x	x	?	x	x	x	x	x	x	x	S	?	S	S	x	x	s	S	22	4I
S	s	x	S	S	s	s	s	x	x	s	s	x	x	x	S	S	S	S	x	x	S	x	x	x	s	x	x	23	6G
x	x	x	x	s	x	x	S	x	s	s	x	x	x	x	x	x	x	s	x	x	x	x	x	x	S	x	x	24	1J
–	x	x	s	x	S	S	S	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	s	S	x	x	25	2F
x	–	x	x	x	s	s	s	x	x	x	x	S	x	S	x	x	x	x	S	S	x	S	x	x	x	x	x	26	6I
x	x	–	x	x	?	s	s	x	x	x	x	?	x	x	x	x	x	x	x	s	?	s	S	S	x	s	S	27	4B
s	x	x	–	S	S	S	s	x	x	S	x	x	x	x	s	x	x	s	x	x	x	x	x	s	S	x	x	28	2D
x	x	x	S	–	x	x	S	x	x	x	x	x	S	s	s	S	S	s	x	x	x	x	x	x	x	x	x	29	1A
S	s	?	S	x	–	s	s	?	s	s	x	s	x	?	S	x	S	S	S	?	s	S	x	x	s	?	?	30	6H
S	s	s	S	x	s	–	s	x	s	x	s	x	x	S	s	x	s	x	S	s	x	s	x	x	s	x	x	31	6B
S	s	s	s	S	s	s	–	x	s	x	x	x	x	x	x	x	x	s	x	x	x	x	x	x	x	x	x	32	6D
x	s	x	x	x	?	x	x	–	x	x	x	?	x	x	x	x	x	x	S	s	?	S	S	x	x	x	x	33	3I
x	s	x	x	x	s	s	s	x	–	x	s	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	34	6J
x	x	x	S	s	x	x	x	x	x	–	x	x	s	x	x	x	x	x	x	x	x	x	x	x	x	x	x	35	1G
x	s	x	x	x	s	s	s	x	s	x	–	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	36	6F
x	S	?	x	x	s	x	x	?	x	x	x	–	x	?	S	s	S	x	s	?	s	s	s	S	x	?	?	37	5H
s	x	x	s	S	x	x	x	x	x	s	x	x	–	x	s	x	s	x	S	x	x	x	x	s	x	x	x	38	2G
x	S	x	x	s	?	S	x	s	x	x	x	?	x	–	s	x	S	x	s	s	?	S	S	S	s	x	s	39	3A
s	x	x	s	s	S	S	x	x	x	x	x	S	s	s	–	x	s	x	x	x	s	S	S	s	x	x	x	40	2A
x	s	x	x	S	x	x	x	s	x	x	x	s	x	x	x	–	x	x	s	x	x	s	x	x	x	x	x	41	5I
s	x	s	s	S	S	s	x	x	x	x	x	S	s	S	s	x	–	x	x	s	s	s	S	s	x	x	S	42	2B
x	x	x	s	s	S	x	x	x	x	x	x	x	x	x	x	x	x	–	x	x	x	x	x	x	x	x	x	43	1D
x	S	x	x	s	S	s	x	S	x	x	x	s	S	s	s	s	s	x	–	x	x	s	s	x	x	x	x	44	5A
x	S	s	x	x	?	s	s	s	x	x	x	?	x	s	x	x	x	x	x	–	?	s	S	x	x	x	s	45	3B
s	x	?	s	x	s	x	x	?	x	x	x	s	s	?	s	x	x	x	x	?	–	x	x	s	x	?	?	46	2H
x	S	s	x	x	S	s	x	S	x	x	x	s	x	S	S	s	s	x	s	s	x	–	s	x	x	x	x	47	5B
x	x	S	x	x	x	x	x	S	x	x	x	s	x	S	S	s	s	x	x	S	x	s	–	s	x	s	x	48	5C
s	x	S	s	x	x	x	x	x	x	x	x	S	s	S	s	x	x	x	x	x	s	x	s	–	x	s	s	49	2C
S	s	x	S	s	s	s	s	x	x	x	s	x	x	s	x	x	x	x	s	x	x	x	x	x	–	x	x	50	6A
x	x	s	x	x	?	x	x	x	x	x	x	?	x	x	x	x	x	x	x	x	?	x	s	s	x	–	s	51	4C
x	x	S	x	x	?	x	x	s	x	x	x	?	x	s	x	x	S	x	x	s	?	x	s	s	x	s	–	52	3C

The reaction (1) proceeds toward the right side because the $KClO_4$ has the minimum solubility of all. This reaction creates very dangerous ammonium chlorate which easily causes a spontaneous decomposition. On the other hand, the reaction (2) causes no reaction because $KClO_3$ at the left side has the minimum solubility of all. These are to explain the German regulation forbids the mixture of potassium chlorate and ammonium salts, but allows that of potassium chlorate and ammonium chloride.[2]

With the reactions of ammonium perchlorate and nitrates in the same way we find:

$$NH_4ClO_4 \ (6C) \quad + KNO_3 \ (1A) \ \rightarrow$$
$$\qquad 29.9 \qquad\quad 45.6$$

$$\qquad NH_4NO_3 \,(6A) \ + \ KClO_4 (1C)\downarrow$$
$$\qquad\qquad 238 \qquad\qquad\quad 2.6 \qquad (3)$$

$$2\,NH_4ClO_4 \quad (6C) \ + \ Ba(NO_3)_2 \ (4A)\downarrow\leftarrow$$
$$\quad 29.9 \qquad\qquad\qquad 11.4$$

$$\qquad 2\,NH_4NO_3 \ (6A) \ + \ Ba(ClO_4)_2 \ (4C)$$
$$\qquad\qquad 238 \qquad\qquad\quad 320 \qquad (4)$$

(3) and (4) explain our experiences: when ammonium perchlorate is mixed with potassium nitrate, the mixture gradually absorbs moisture in the air to become muddy due to the high hygroscopic nature of the ammonium nitrate. On the other hand, when ammonium perchlorate is mixed with barium nitrate, no reaction occurs. The reason is that the reaction (3) proceeds to the right due to the formation of $KClO_4$ which has the minimum solubility, while the latter (4) stops in the left due to the minimum solubility of $Ba(NO_3)_2$.

2.2. Dichromate Reactions

A special attention should be paid with reactions of dichromate to apply the minimum solubility law. Dichromate salts are important to protect metals, especially magnesium, from corrosion. With ammonium perchlorate the reaction proceeds as follows:

$$K_2Cr_2O_7 \quad + \ 2\,NH_4ClO_4 \quad \rightarrow$$
$$\ 19.1 \qquad\qquad 29.9$$

$$\qquad 2\,KClO_4\downarrow \ + \ (NH_4)_2Cr_2O_4 \quad (5)$$
$$\qquad\quad 2.6 \qquad\qquad 46.5$$
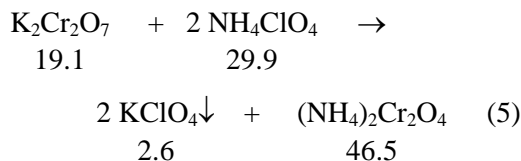
In this case the reaction proceeds in the same way as the reaction (1). This is an ordinary reaction which follows the minimum solubility law. (In this reaction the volume of the right side mixture increases five percents from the left. Therefore, it is better to use the ammonium dichromate in place of the potassium dichromate to avoid cracking of stars during the store.) However, when using dichromates, they often create acid. The values of solubility of materials in acid are not always clear. In such cases, the direction of degeneration reaction must be experimentally confirmed. Examples are shown as follows (the solubilities noted are the values in water):

$K_2Cr_2O_7$	+	$Sr(NO_3)_2$	+	H_2O	$\rightarrow$	K_2CrO_4	+	$SrCrO_4\downarrow$	+	$2\,HNO_3$	(6)
18.1		88.7				66.1		0.096			
$K_2Cr_2O_7$	+	$SrSO_4\downarrow$	+	H_2O	$\leftarrow$	K_2CrO_4	+	$SrCrO_4$	+	H_2SO_4	(7)
18.1		0.00138				66.1		0.096			
$K_2Cr_2O_7$	+	$SrCO_3\downarrow$	+	H_2O	$\leftarrow$	K_2CrO_4	+	$SrCrO_4$	+	H_2CO_3	(8)
18.1		0.00090				66.1		0.096			
$K_2Cr_2O_7$	+	$Ba(NO_3)_2$	+	H_2O	$\rightarrow$	K_2CrO_4	+	$BaCrO_4\downarrow$	+	$2\,HNO_3$	(9)
18.1		11.5				66.1		0.00046			
K_2CrO_7	+	$BaSO_4\downarrow$	+	H_2O	$\leftarrow$	K_2CrO_4	+	$BaCrO_4$	+	H_2SO_4	(10)
18.1		0.0029				66.1		0.00046			
$K2CrO_7$	+	$BaCO_3$	+	H_2O	$\rightarrow$	K_2CrO_4	+	$BaCrO_4\downarrow$	+	H_2CO_3	(11)
18.1		+.0022				66.1		0.00046			
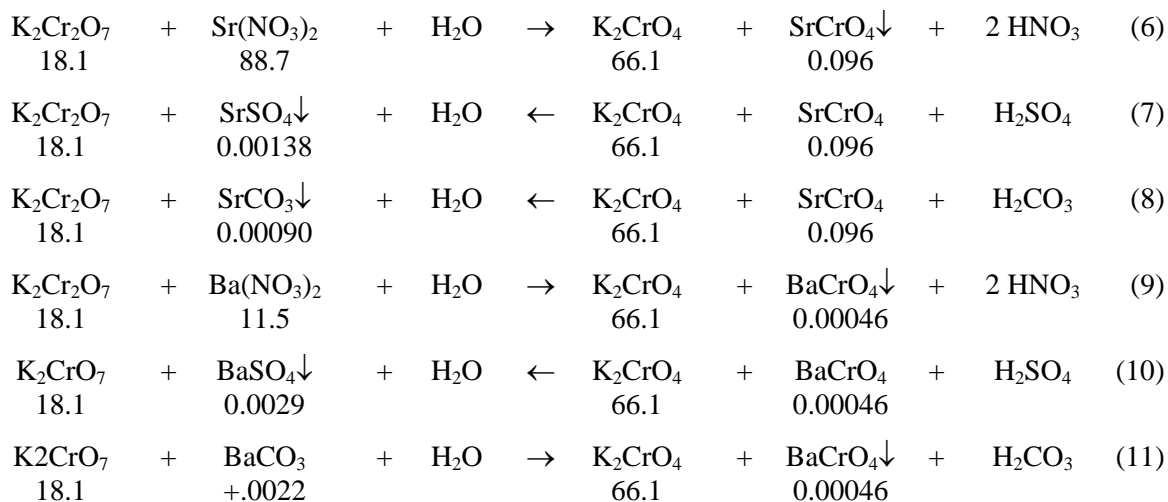
Of these reactions, (7), (8), (9) and (11) follow the minimum solubility law in water, (6) follows the law when the mixture is alkaline, and (10) does not follow experimentally.

3. A New Chemical Method of Magnesium Coating

3.1. Preliminary Experiment with Potassium Dichromate

The author tested with various consolidated mixtures to see the effect of potassium dichromate on magnesium from 1980 to 1987. The sample compositions are shown in Table 2.

Table 2. Sample Compositions for Preliminary Test.

(1) Base composition	A	B	C	D	E	F	G	H	I
Mg	30%	20%	30%	30%	30%	40%	23%	20%	–%
Mg–Al(50/50)	—	—	—	—	—	—	—	—	25
NH_4ClO_4	50	60	60	60	60	50	60	60	60
$SrSO_4$	20	20	—	—	—	—	—	—	—
$CaSO_4$	—	—	10	—	—	—	—	—	—
$NaNO_3$	—	—	—	10	—	—	—	—	—
Na_2SO_4	—	—	—	—	10	10	—	—	—
$BaSO_4$	—	—	—	—	—	—	17	—	—
$Ba(NO_3)_2$	—	—	—	—	—	—	—	20	15
(2) Sample composition	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9
Base composition	A	B	C	D	E	F	G	H	I
$K_2Cr_2O_7$ (add'l. %)	5	5	5	5	5	5	5	5	5
(3) Sample composition	No. 10	No. 11	No. 12	No. 13	No. 14	No. 15	No. 16	No. 17	No. 18
Base composition	A	B	C	D	E	F	G	H	I
$K_2Cr_2O_7$ (add'l. %)	5	5	5	5	5	5	5	5	5
Guanidine nitrate (add'l %) $C(NH)(NH_2)_2 \cdot HNO_3$	10	10	10	10	10	10	10	10	10

Note: 1. Magnesium powder passed 80 mesh, manufactured by Mitsuwa Kinzoku Co., Magnalium passed 100 mesh, manufactured by Tachikawa Yozai Co. These were coated with 5% potassium dichromate before the mixing.

2. Other chemicals were first class reagents except the guanidine nitrate.

3. Guanidine nitrate was used after recrystalization from the product by Chugoku-Kayaku Co.

100 grams of each mixture were consolidated with 10% nitrocellulose solution in acetone in a form of cut star of 8 mm cube.

The sample stars were placed naturally for years in a room of our laboratory without air conditioning. The results of degeneration are shown in Table 3 and Figure 1.

Table 3 The Results of Degeneration (After Seven Years and Ten Months).

Sample composition	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9
Exterior view	f	c	w+c	g	g	g+c	g+f	w	g+c
Ignition	no	no	no	no	no	no	no	no	no
Sample Composition	No. 10	No. 11	No. 12	No. 13	No. 14	No. 15	No. 16	No. 17	No. 18
Exterior view	g	g	g	b	b	b	g	w+c	g
Ignition	i	i	i	no	i	i	i	no	no

Note: Symbols: f: a white substance oozed out of the surface to form white flecks,

c: cracked,

w+c: became white and cracked,

g: became gray,

g+c: became gray and cracked,

w: became white,

g+f: became gray and a white substance oozed out of the surface,

b: became black,

i: ignited with black match and blinked,

no: no ignition with black match.

The initial view of all the stars was brownish gray. In spite of the long time store of about eight years, the compositions Nos. 10, 11, 12, 14, 15 and 16 were still vivid and others all died.

3.2. Experimental Research with the Foregoing Effect

In combination of Table 2 with Table 3, the difference between the vivid and died is that the compositions of the former contain some sulfate, while those of the latter no sulfate. Sulfates should be the most important material to avoid corrosion of magnesium.

The next important material should be guanidine nitrate because the sample compositions were not vivid without this material (see compositions Nos. 1–9).

Magnesium or some times magnalium, ammonium perchlorate and potassium dichromate were common to all compositions. To protect magnesium from corrosion, some dichromate is thought to be chemically the most effective from our experiences and ammonium perchlorate is the strongest enemy against magnesium when we plan firework compositions.

From above considerations, three materials, some sulfate, guanidine nitrate and some dichromate, in combination may be chemically the most effective for the magnesium coating. To make this point more clear, the following experiment was carried out.

Several pieces of magnesium ribbon for chemical use (0.2 mm thick and 3 mm wide) were soaked in saturated sulfate and ammonium dichromate solutions in water in test tubes and were observed. As the sulfates, K_2SO_4, Na_2SO_4, $(NH_4)_2SO_4$, $MgSO_4$ and $Al_2(SO_4)_3$ were used and as the dichromate $(NH_4)_2Cr_2O_7$ was used. At the beginning tiny bubbles were formed on the surface of the magnesium ribbon. Then the surface changed its color silver to brown and then black, and the generation of the bubble ceased. During the bubble generation the pieces of the ribbon rose to the surface of the solution. Therefore, it was stirred at intervals to sink them. The reaction took about 24 hours to complete perfectly the black film on the surface of the ribbon. Only the ammonium sulfate did not make a good film: it looked as if the film exfoliated in the solution during the reaction.
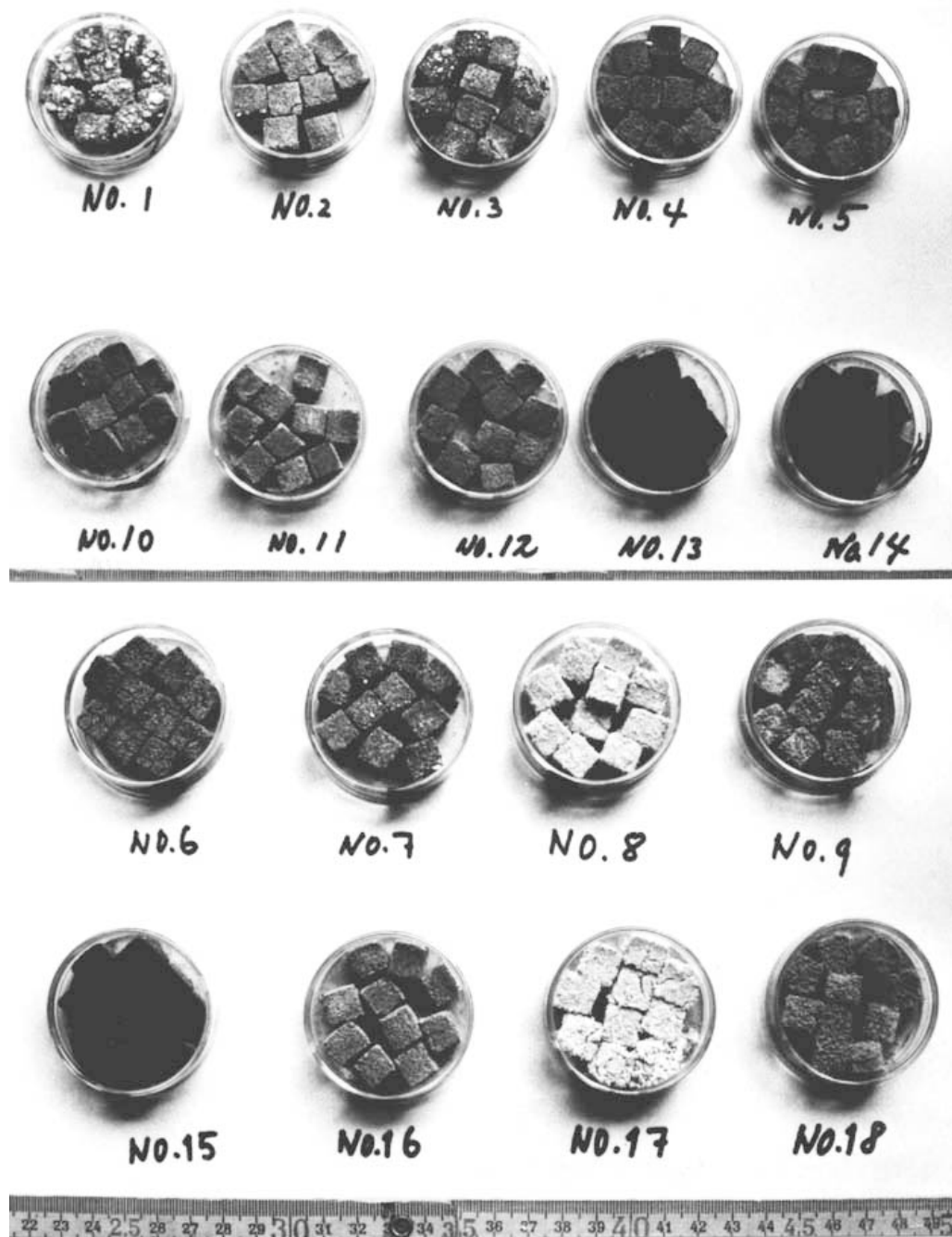
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Figure 1. The appearance of sample stars after a long store of seven years and ten months.

Then a corrosion test was carried out with the magnesium ribbon pieces coated with the black film. They were soaked in a saturated ammonium perchlorate solution in water and left for hours. The pieces from potassium sulfate, sodium sulfate, magnesium sulfate and aluminum sulfate were not attacked by the solution after three and a half days except making few pinholes. Those from ammonium sulfate were fairly attacked and at last dissolved in the solution continually generating small bubbles. (Figure 2)
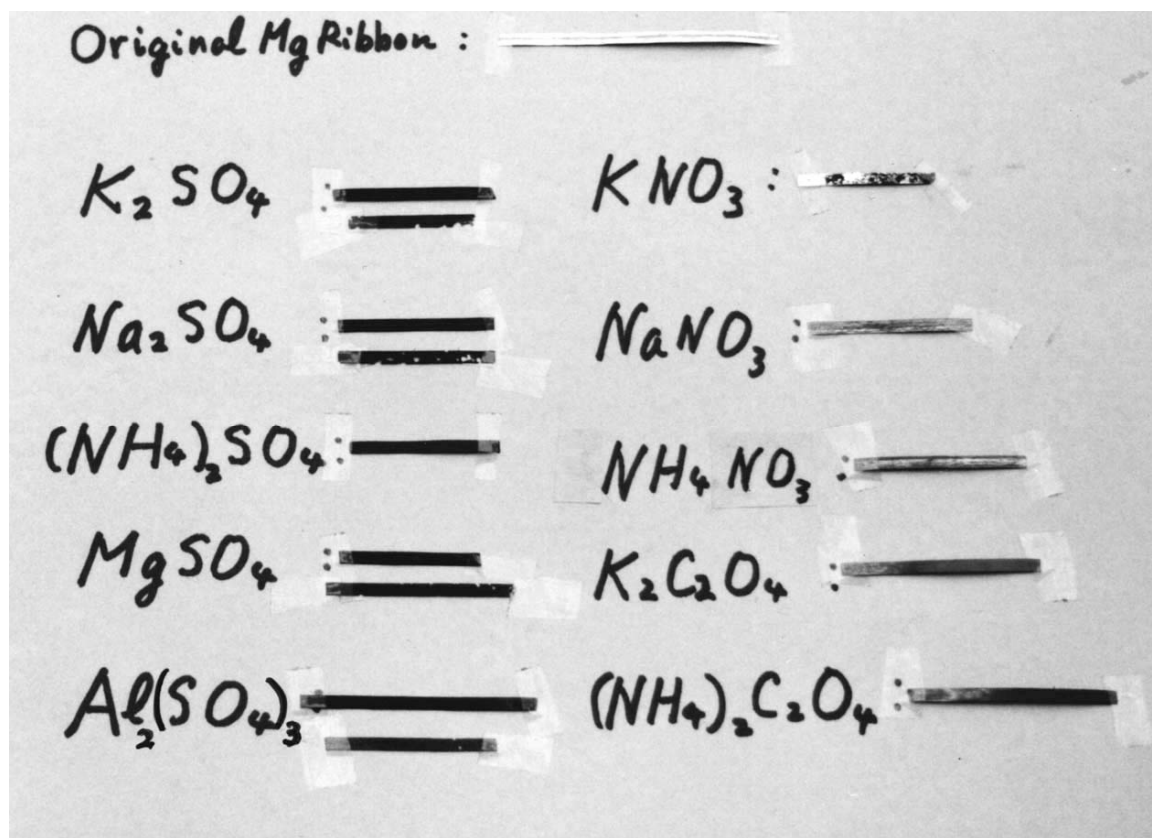
Figure 2. Results of chemical coating on magnesium ribbon pieces using saturated solution of sulfates, nitrates and oxalates with ammonium dichromate.

Note: For each sample, the upper piece is of no corrosion test, the lower passed corrosion test in a saturated solution of ammonium perchlorate in water, and shows few tiny pinholes. There are no lower samples with nitrates and oxalates because they are all dissolved at the corrosion test. The same is true for ammonium sulfate.

It is seen from the above experiment the black film is very effective to protect magnesium from corrosion caused by ammonium perchlorate. For comparison, with other materials, KNO_3, $NaNO_3$, NH_4NO_3, $K_2C_2O_4$ and $(NH_4)_2C_2O_4$, the same experiment as above was carried out. All of them did not give the black film, but only the oxalates gave a thin brown film. At the corrosion test the magnesium pieces after the soaking all dissolved in the ammonium perchlorate solution without resistance.

The principle of making the black film which is very corrosion resistant against ammonium perchlorate is thought to be as follows. The magnesium ribbon pieces in the sulfate solution generate hydrogen gas as tiny bubbles reacting with the sulfate very slowly. The values of pH of the solution were 3.5–4.0 which showed slight acidity at the test. Then the dichromate is reduced by the hydrogen to CrO_2 which forms the black film on the surface of the magnesium ribbon pieces. The reducing reaction of the nitrates or oxalates is very weak and they cannot form the black film in a short time. It is understood from the phenomenon that the ribbon pieces rose to the surface of the solution by the buoyancy of the hydrogen bubbles when using sulfates, but when the nitrates or oxalates were used, the phenomenon was not intensive, although the values of pH of the solution were the same as those of the former.

The black film is formed with only sulfate and dichromate. Therefore, it looks as if there were no use of guanidine nitrate. From the results in Table 3, however, this material plays an important role to give the corrosion resistance

to the film, because the ignitions occurred only when the compositions contained guanidine nitrate (Table 2, 3, Nos. 10–12 and Nos. 14–16). Soaking tests of the magnesium ribbon in three component solutions of magnesium sulfate, ammonium dichromate and guanidine nitrate in various ratios (Figure 3) were carried out. (Magnesium sulfate was selected from other sulfates because it seemed as it was the most effective in forming the black film.) The figures in Figure 3 show the weight decrease of the sample pieces during the soaking in the solution for 28 hours. From this result it is thought that guanidine nitrate suppresses the reaction of magnesium. The effect is the largest when the value of the percentage of guanidine nitrate is 10% of all materials. The author observed that black film which was formed without such suppression

caused exfoliation from the surface of the magnesium ribbon to a black powder, and at the corrosion test the ribbon pieces showed very poor effect.

The tests above described were practiced at room temperatures. On the other hand, several tests were carried out at 80 °C; however, the effects were not good.

From the results described above it is concluded that the reaction to form the black film on the magnesium surface must be slow at ordinary temperatures using a mixture of proper ratio of guanidine nitrate, some sulfate except ammonium sulfate, and some dichromate.

The results of this section will be reasonably connected with those of the foregoing experi-
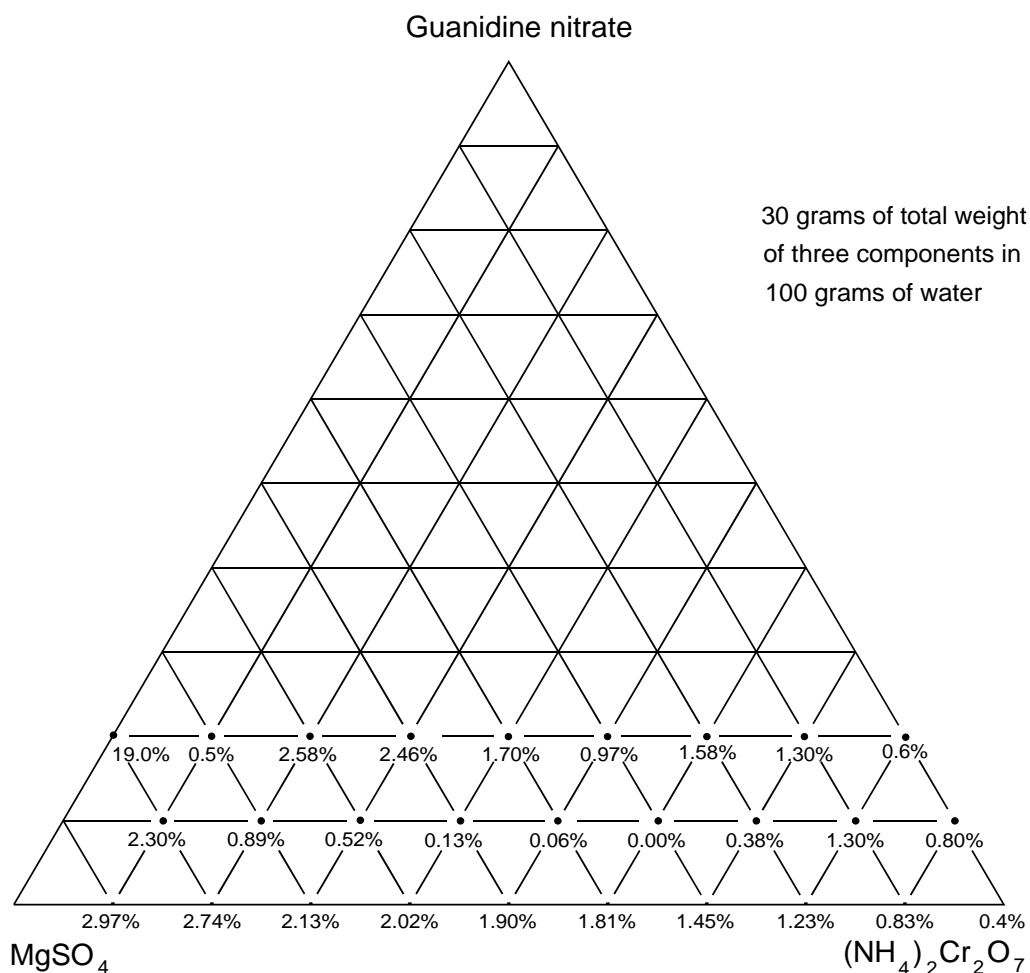
Figure 3. Weight decrease of magnesium ribbon pieces after soaking in guanidine nitrate, magnesium sulfate and ammonium dichromate solution in water for 28 hours.

ment in 3.1. In Figure 1 the stars without guanidine nitrate (Nos. 1–9) were more degenerate than those with it as it is seen with the white spots on the surface of the former only. Nos. 8, 9, 17, and 18, which contained barium nitrate that damaged the potassium dichromate, belong to an exceptional case. Nos. 13, 14 and 15 have a very deep black surface, which may be the same with the black film of this section. However, only No. 13 which contained sodium nitrate in place of sodium sulfate was not vivid. Even the sodium nitrate can form a black film when the star is stored for such a long time. However the film is weaker than that from a sulfate. Other stars which contained guanidine nitrate, Nos. 10, 11, 12 and 16, are covered with a gray surface which shows it is still in the midst of forming the black film due to the low solubility of each sulfate.

3.3. The New Practical Method of Coating Magnesium Powder

Considering above experiments, the author presents the following coating method: 220 g of a hydrate of magnesium sulfate, $MgSO_4 \cdot 7H_2O$, 90 g of ammonium dichromate, $(NH_4)_2Cr_2O_7$, and 20 g of guanidine nitrate, $CN_3H_5 \cdot HNO_3$, are dissolved in 500 cc of water. 1000 g of magnesium powder is placed in a fairly large aluminum bowl and the solution is added to it. It is mixed, stirring by hand with gloves, until the powder colors uniformly brown. Then the powder is spread on a sheet of Kraft paper and dried well in the sun. When dried, it is passed through a 30 mesh sieve. The dust must not be inhaled because ammonium dichromate is poisonous.

With this method, the resistant black film is not formed in a short time even when the powder is soaked in a larger volume of the solution than the above. However, when the coating materials exist together with the magnesium powder, this method was far more effective at a corrosion test against ammonium perchlorate than the mechanical coatings using paraffin, linseed oil or polyester, which gave only a short time resistance of a few seconds or minutes.

4. Discussion and Conclusion

(1) The author presented the "minimum solubility law", having an idea that the chemical reactions or degenerations inside of a consolidated firework mixture may be thought of as it is those among substances of a highly concentrated solution in water.

(2) The number of ions which can move in a consolidated mixture will be so small that the reactions proceed very slowly. Therefore, it has been very difficult to foresee the direction of reaction without experiences. However, with the help of this law we could overcome the difficulty.

(3) However, this method may not be applied to substances which do not dissolve into ions, metals or to acid or alkali forming substances, the solubilities of which in the acid or alkali are unknown.

(4) All the materials arranged in Table 1 are thought to have some relation in the firework field. The reactions with symbols are not all experimentally confirmed, but a few.

(5) Considering the results of two experiments, the foregoing of about eight year store and the latter supplemental, a method of new chemical coating of magnesium powder is presented: it is to use some sulfate which is easily soluble in water, except ammonium sulfate, some dichromate, and guanidine nitrate. The former two create a black film of CrO_2 and the latter makes the film stick well to the surface of magnesium grains adjusting the reaction rate.

(6) At the experiments with magnesium ribbon pieces, the coating was completed in one day soaking. However, with a magnesium powder, the reaction was very slow and takes more and more time. Therefore, it is better to cover the grains with a concentrated solution of the three materials in a proper ratio and to dry in the sun, as it is in ordinary case of coating. The temperatures must not be warm. The black film may be created during the store very slowly after the coating. It is still effective when the materials are not removed from the grains.

(7) The difference between the chemical coating and the ordinary physical coating may be: the former makes a resistant film in the course of the coating operation or later gradually makes it slowly in the course of the store, and the latter makes it only in the course of the operation. Experiments showed the former was far more effective than the latter by ordinary physical methods.

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