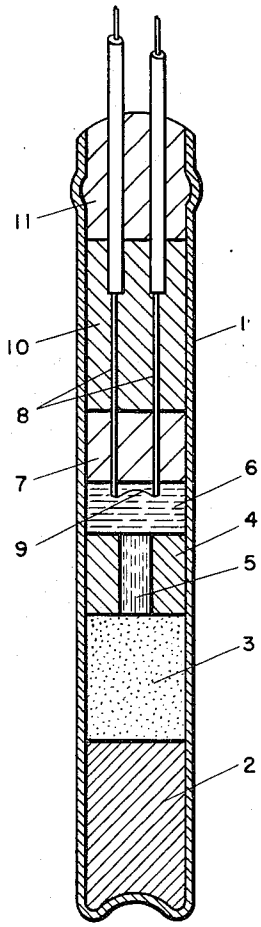
Sept. 4, 1956 D. T. ZEBREE 2,761,386

ELECTRIC INITIATOR AND IGNITION MIXTURE THEREFOR

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ELECTRIC INITIATOR AND IGNITION MIXTURE THEREFOR

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13 Claims. (Cl. 102—28)

This invention relates to blasting initiators and more particularly to ignition compositions and initiators employing such compositions.

For many years mixtures of finely divided lead and selenium have been employed in the electric initiator art with very satisfactory results. As the initiator art developed, it became apparent, however, that this generally satisfactory composition was characterized by certain deficiencies which it has been desirable to correct. For example, it has been discovered that failures in regular delay blasting initiators resulting from the oxidation of lead in the lead-selenium mixture could be overcome by the addition to the mixture of certain amounts of aluminum, antimony, antimony phosphide, boron, cadmium, carbon, iron, magnesium, nickel, phosphorus, and silicon. These improved mixtures are disclosed in copending application Serial No. 78,383, filed February 25, 1949.

Although the addition of such modifiers was found to eliminate overlapping of delay periods in regular delays, that is, delay initiators in which the period between application of current and the firing of the cap is measured in terms of a second or more, the lead-selenium mixtures and the modified lead-selenium mixtures of application Serial No. 78,383 are still characterized by an undesirable lack of uniformity in firing time when employed in short period delay caps wherein the period of delay is measured in terms of milliseconds.

While lead-selenium ignition compositions are generally characterized by satisfactory resistance to premature firing by static discharge, it would, of course, be desirable to increase this resistance to static discharge if such increase can be effected without adversely affecting the otherwise acceptable performance of the mixture. In like manner, it would be desirable to improve the charging characteristics of a lead-selenium mixture since such mixtures are normally quite dusty. As in the case of any ignition composition which is employed with high explosive materials, it is desirable to increase the impact sensitivity of the mixture in so far as it is possible

without adversely affecting the ignition characteristics of the composition.

Now in accordance with the present invention, compositions predominantly comprising mixtures of lead and selenium can be prepared which have increased resistance to ignition by static discharge, which have better flowing and charging characteristics, which have lower impact sensitivity, and which, when employed in short period delay initiators, bring about considerably greater uniformity in firing time.

Generally described, the present invention is an ignition composition for electric initiators which comprises lead-selenium and a minor amount of a metal salt of a long chain fatty acid. It has been found that the presence of a suitable amount of such metallic soaps in mixture predominantly comprising lead and selenium effects highly desirable changes in terms of uniformity of firing time, particularly in short period delay initiators, static resistance, charging ease, and friction and impact sensitivity without detracting from the other widely accepted characteristics of lead-selenium mixtures. While the metal salts of the long chain fatty acids are generally operable, the stearates, oleates, laurates, and palmitates of such metals as lead, cadmium, iron, magnesium, aluminum, and zinc are most readily available and are preferred. Of all of these compounds lead stearate is especially preferred. While the mixtures of this invention are especially adapted for use in short period delay initiators, they may be used as well in instantaneous and regular delay initiators.

The effect of the presence of metallic soaps in lead-selenium on uniformity of firing times of short period delay caps is shown in Table I. The caps employed are illustrated in the drawing and comprise a bronze shell **1** containing a pressed base charge **2** of 0.24 g. of pentaerythritol tetranitrate. A priming charge **3** of 0.38 g. of diazodinitrophenol/potassium chlorate (75/25) was pressed on top of the base charge. A delay fuse consisting of a load tube **4** containing a core **5** of barium peroxide/selenium (70/30) is pressed on the priming charge. A loose charge **6** of ignition composition in accordance with the invention is loaded on top of the fuse. An ignition plug **7** is inserted over the ignition composition. Lead wires **8** pass through the ignition plug into the ignition composition and are connected at their terminals by a bridge wire **9** which is surrounded by the ignition composition. A layer of waterproofing **10** and a sulfur seal **11** complete the initiator.

In the test recorded in Table I, the indicated number of caps was separately fired and the elapsed time (measured in milliseconds) between application of the firing current and the firing of the cap was measured for each. A firing current of 2 amperes was employed. Unless otherwise indicated, a chemically equivalent mixture of lead and selenium was employed (Pb-Se—72.4/27.6).

Table I

Example No.	Ignition Mixture	No. Timed	Firing Time Data		
			Range (ms.)	Spread	Average
1	Pb-Se (Control)	10	380-480	100	420
2	Pb-Se/Si, 98/2 (Control)	20	400-520	120	455
3	Pb-Se/lead stearate, 99.8/0.2	10	380-430	50	400
4	Pb-Se/lead stearate, 99.5/0.5	10	340-370	30	360
5	Pb-Se/lead stearate, 99.0/1.0	10	320-390	70	345
6	Pb-Se/lead stearate, 98.0/2.0	10	310-340	30	325
7	Pb-Se/lead stearate, 97.0/3.0	10	380-430	50	400
8	Pb-Se/lead stearate, 96.5/3.5	10	340-400	60	366
9	Pb-Se/lead stearate, 96.0/4.0	10	360-420	60	394
10	Pb-Se/lead stearate, 95.0/5.0	10	370-410	40	390
11	Pb-Se/lead stearate, 94.0/6.0	10	420-460	40	437
12	Pb-Se/lead stearate, 93.5/6.5	8	460-520	(1)	(1)
13	Pb-Se(80-20)/lead stearate, 98.5/1.5	10	340-400	60	362
14	Pb-Se(64-36)/lead stearate, 98.5/1.5	10	310-360	50	336
15	Pb-Se(80-20)/Si/lead stearate, 97.5/1.0/1.5	10	320-410	90	355
16	Pb-Se(64-36)/Si/lead stearate, 97.5/1.0/1.5	10	330-360	30	349
17	Pb-Se/Si/lead stearate, 98.8/1.0/0.2	9	330-440	110	382
18	Pb-Se/Si/lead stearate, 98.5/1.0/0.5	10	320-420	100	366
19	Pb-Se/Si/lead stearate, 98.0/1.0/1.0	10	390-440	50	411
20	Pb-Se/Si/lead stearate, 97.5/1.0/1.5	10	310-340	30	324
21	Pb-Se/Si/lead stearate, 97.0/1.0/2.0	10	320-380	60	344
22	Pb-Se/Si/lead stearate, 96.5/1.0/2.5	10	340-370	30	352
23	Pb-Se/Si/lead stearate, 95.7/1.0/3.3	10	350-400	50	372
24	Pb-Se/Si/lead stearate, 95.5/1.0/3.5	6	460-480	(1)	(1)
25	Pb-Se/Si/calcium stearate, 98.8/1.0/0.2	10	370-450	80	404
26	Pb-Se/Si/calcium stearate, 98.5/1.0/0.5	10	360-370	10	367
27	Pb-Se/Si/calcium stearate, 98.0/1.0/1.0	10	340-380	40	357
28	Pb-Se/Si/calcium stearate, 97.5/1.0/1.5	10	330-380	50	352
29	Pb-Se/Si/calcium stearate, 96.5/1.0/2.5	10	370-470	100	396
30	Pb-Se/Si/calcium stearate, 95.5/1.0/3.5	10	410-470	60	428
31	Pb-Se/Si/calcium stearate, 95.3/1.0/3.7	10	370-420	50	393
32	Pb-Se/Si/calcium stearate, 95.0/1.0/4.0	5	480-540	(1)	(1)
33	Pb-Se/Si/iron stearate, 98.8/1.0/0.2	10	340-450	110	398
34	Pb-Se/Si/iron stearate, 98.5/1.0/0.5	10	360-420	60	377
35	Pb-Se/Si/iron stearate, 98.0/1.0/1.0	9	360-380	20	376
36	Pb-Se/Si/iron stearate, 97.5/1.0/1.5	10	310-330	20	320
37	Pb-Se/Si/iron stearate, 96.5/1.0/2.5	10	360-420	60	392
38	Pb-Se/Si/iron stearate, 96.0/1.0/3.0	10	330-400	70	365
39	Pb-Se/Si/iron stearate, 95.5/1.0/3.5	9	390-440	(1)	(1)
40	Pb-Se/Si/magnesium stearate, 98.9/1.0/0.1	10	380-440	60	409
41	Pb-Se/Si/magnesium stearate, 98.8/1.0/0.2	10	410-460	50	430
42	Pb-Se/Si/magnesium stearate, 98.7/1.0/0.3	10	370-440	70	406
43	Pb-Se/Si/magnesium stearate, 98.5/1.0/0.5	10	400-460	60	428
44	Pb-Se/Si/magnesium stearate, 98.0/1.0/1.0	10	380-410	30	398
45	Pb-Se/Si/magnesium stearate, 97.5/1.0/1.5	10	320-360	40	344
46	Pb-Se/Si/magnesium stearate, 97.0/1.0/2.0	10	400-430	30	418
47	Pb-Se/Si/magnesium stearate, 96.7/1.0/2.3	10	320-370	50	351
48	Pb-Se/Si/magnesium stearate, 96.5/1.0/2.5	1	(1)	(1)	(1)
49	Pb-Se/Si/zinc stearate, 98.8/1.0/0.2	10	340-370	30	378
50	Pb-Se/Si/zinc stearate, 98.5/1.0/0.5	10	320-400	80	343
51	Pb-Se/Si/zinc stearate, 98.0/1.0/1.0	10	380-450	70	417
52	Pb-Se/Si/zinc stearate, 97.5/1.0/1.5	10	320-350	30	335
53	Pb-Se/Si/zinc stearate, 96.5/1.0/2.5	10	340-370	30	351
54	Pb-Se/Si/zinc stearate, 95.0/1.0/4.0	10	430-500	70	455
55	Pb-Se/Si/zinc stearate, 94.5/1.0/4.5	2	[1] 720	(1)	(1)
56	Pb-Se/Si/aluminum laurate, 98.8/1.0/0.2	10	390-430	40	410
57	Pb-Se/Si/aluminum laurate, 98.5/1.0/0.5	10	320-440	80	361
58	Pb-Se/Si/aluminum laurate, 98.0/1.0/1.0	10	330-360	30	347
59	Pb-Se/Si/aluminum laurate, 97.5/1.0/1.5	10	340-380	40	356
60	Pb-Se/Si/aluminum laurate, 96.5/1.0/2.5	10	350-400	50	373
61	Pb-Se/Si/aluminum laurate, 95.5/1.0/3.5	10	380-400	20	391
62	Pb-Se/Si/aluminum laurate, 95.0/1.0/4.0	10	420-460	40	438
63	Pb-Se/Si/aluminum laurate, 94.0/1.0/5.0	10	360-410	50	375
64	Pb-Se/Si/aluminum laurate, 93.5/1.0/5.5	10	370-460	90	419
65	Pb-Se/Si/aluminum laurate, 93.0/1.0/6.0	5	450-500	(1)	(1)
66	Pb-Se/Si/calcium oleate, 98.8/1.0/0.2	10	360-450	90	397
67	Pb-Se/Si/calcium oleate, 98.5/1.0/0.5	10	300-360	60	346
68	Pb-Se/Si/calcium oleate, 98.0/1.0/1.0	10	340-380	40	360
69	Pb-Se/Si/calcium oleate, 97.5/1.0/1.5	10	320-380	60	350
70	Pb-Se/Si/calcium oleate, 97.0/1.0/2.0	9	340-380	40	376
71	Pb-Se/Si/calcium oleate, 96.5/1.0/2.5	10	340-400	60	358
72	Pb-Se/Si/calcium oleate, 96.0/1.0/3.0	10	360-420	60	376
73	Pb-Se/Si/calcium oleate, 95.5/1.0/3.5	10	280-350	70	315
74	Pb-Se/Si/calcium oleate, 95.0/1.0/4.0	10	360-410	50	392
75	Pb-Se/Si/calcium oleate, 94.0/1.0/5.0	10	340-380	40	361
76	Pb-Se/Si/calcium oleate, 93.0/1.0/6.0	10	310-380	70	346
77	Pb-Se/Si/calcium oleate, 92.0/1.0/7.0	10	320-410	90	373
78	Pb-Se/Si/calcium oleate, 91.5/1.0/7.5	1	(1)	(1)	(1)

[1] Bridge wire fused in one cap but ignition powder did not ignite. Failure was due to desensitization of the ignition powder by the metallic soap.

The influence of the metallic soaps on static resistance of lead-selenium mixtures is shown in Table II. In these tests, static potential was applied between shunted leg wires and shell in accordance with the conventional static testing procedure employed by the initiator art. The caps were similar to that shown in the drawing. The lead and selenium were in stoichiometric proportions. In evaluating the data in this table, it should be observed that the actual energy needed to fire a cap by electrostatic discharge is proportional to the square of the firing voltage. Thus, in two cases where 1000 and 2000 volts, respectively, are required to cause ignition, the latter case involved four times as much energy as the first.

Table II

Example No.	Ignition Mixture	Condenser (mmf.)	M.N.F.V.[1]
79	Pb-Se/Si, 98/2	100	4,000
80	Pb-Se/Si, 98/2	750	1,000
81	Pb-Se/Si, 98/2	3,000	1,000
82	Pb-Se (alone)	750	1,000
83	Pb-Se/lead stearate, 99.5/0.5	100	6,000
84	Pb-Se/lead stearate, 99.5/0.5	750	2,000
85	Pb-Se/lead stearate, 99.5/0.5	3,000	1,000
86	Pb-Se/Si/lead stearate, 97.5/2.0/0.5	100	6,000
87	Pb-Se/Si/lead stearate, 97.5/2.0/0.5	750	2,000
88	Pb-Se/Si/lead stearate, 97.5/2.0/0.5	3,000	1,000
89	Pb-Se/Si/lead stearate, 97.5/1.0/1.5	750	2,000
90	Pb-Se/Si/lead stearate, 97.0/1.0/2.0	750	3,000
91	Pb-Se/Si/lead stearate, 96.5/1.0/2.5	750	4,000
92	Pb-Se/Si/calcium stearate, 97.5/1.0/1.5	750	3,000
93	Pb-Se/Si/iron stearate, 97.5/1.0/1.5	750	2,000
94	Pb-Se/Si/magnesium stearate, 97.5/1.0/1.5	750	3,000
95	Pb-Se/Si/zinc stearate, 97.5/1.0/1.5	750	3,000
96	Pb-Se/Si/aluminum laurate, 97.0/1.0/2.0	750	2,000
97	Pb-Se/Si/calcium oleate, 96.0/1.0/3.0	750	2,000

[1] Maximum nonfiring voltage.

The diminution in impact and friction sensitivity effected by addition of the metal soaps is illustrated in Table III. In the experiments recorded, the compositions were tested on a Bureau of Mines impact machine to determine the height and angle necessary to give 50% shots.

Table III

Example No.	Ignition Mixture	Weight, Kg.	Impact Angle (°)	Height for 50% Shots (cm.)
98	Pb-Se(72.4-27.6)/Si, 98/2	2	4	16.
99	Pb-Se(72.4-27.6)/Si, 98/2	4	8	11.
100	Pb-Se(72.4-27.6)/Si/lead stearate, 97.5/2.0/0.5	2	4	41.
101	Pb-Se(72.4-27.6)/Si/lead stearate, 96.5/2.0/1.5	4	4	48.
102	Pb-Se(72.4-27.6)/Si/lead stearate, 96.5/2.0/1.5	4	8	50 [1], 40% shots.
103	Pb-Se(72.4-27.6)/Si/lead stearate, 96.0/2.0/2.0	4	4	50 [1], 7% shots.

[1] Maximum height of test machine; hence, height of fall for 50% shots was over 50 cm.

From the foregoing examples it is apparent that the compositions and initiators of this invention are characterized by highly desirable properties. From the examples in Table I, it will be noted that with a firing current of 2 amperes, failures are obtained when enough metal soap is employed to reduce the ignition sensitivity of the mixture. As will be apparent to those skilled in the art, the concentration at which undesirable ignition sensitivity will be obtained depends on the strength of the firing current employed and on the amount of silicon or other ignition desensitizing additive employed. When employing a firing current of 2 amperes, for example, it has been found that up to 6% of lead stearate may be added to a chemically equivalent lead-selenium mixture without undesirably desensitizing the composition to ignition although between .5 and 2% is preferred. A definite benefit was noted when .2% lead stearate was added.

In order to guard against failures due to formation of lead oxide in the mixture, it is desirable to add silicon or other additive in accordance with application Serial No. 78,383. The amount of metal salt which can be added to a lead-selenium mixture without desensitizing the composition to ignition will depend on the amount of such other additive employed and on the firing current used. With a firing current of 2 amperes and a basic stoichiometric mixture of lead and selenium containing 1% of silicon, it has been found that the following amounts of metal soaps will desirably be added:

Additive	Range Percent	
	Preferred	Overall
Lead stearate	0.5-2.0	0.2-3.3
Calcium stearate	0.5-2.0	0.2-3.7
Iron stearate	0.5-2.0	0.2-3.0
Magnesium stearate	0.5-2.0	0.1-2.3
Zinc stearate	0.5-3.0	0.2-4.0
Aluminum laurate	0.5-3.0	0.2-5.5
Calcium oleate	0.5-5.0	0.2-7.0

Preferred ignition mixtures in accordance with the invention will contain from about 64 to about 80% lead, from about 20 to about 36% selenium, from about .2 to about 2% silicon, and from about 0.5 to about 2% lead stearate.

With respect to static resistance and impact and friction sensitivity, Tables II and III illustrate that the benefits received increased in proportion to the amount of

additive employed. Since the metal soap has a lubricating effect on the powdered lead-selenium mixture, the flowing and charging characteristics of the mixture are markedly improved.

Since various modifications of the invention not specifically set forth herein will occur to those skilled in the initiator art, it is intended that the scope of the invention be limited only by the scope of the appended claims.

What I claim and desire to protect by Letters Patent is:

1. An ignition composition for electric initiators which comprises an ignition mixture of lead and selenium and contains a minor amount of metal salt of a long chain fatty acid.

2. An ignition composition for electric initiators which comprises from about 64 to about 80% lead, from about 20 to about 36% selenium, and a minor amount of metal salt of a long chain fatty acid.

3. An ignition composition for electric initiators which comprises a stoichiometric mixture of lead and selenium and a minor amount of metal salt of a long chain fatty acid.

4. An ignition composition for electric initiators which comprises from about 64 to about 80% lead, from about 20 to about 36% selenium, and a minor amount of metal salt of stearic acid.

5. An ignition composition for electric initiators which comprises from about 64 to about 80% lead, from about 20 to about 36% selenium, and a minor amount of metal salt of lauric acid.

6. An ignition composition for electric initiators which comprises from about 64 to about 80% lead, from about 20 to about 36% selenium, and a minor amount of metal salt of oleic acid.

7. An ignition composition for electric initiators which comprises from about 64 to about 80% lead, from about 20 to about 36% selenium, and a minor amount of lead stearate.

8. An ignition composition for electric initiators which comprises from about 64 to about 80% lead, from about 20 to about 36% selenium, and additive amounts of from about .2 to about 2% silicon, and from about .5 to about 2.0% of lead stearate.

9. An electric blasting initiator having in combination an ignition assembly containing a bridge wire and a loose ignition mixture disposed about the bridge wire which comprises an ignition mixture of lead and selenium and contains a minor amount of metal salt of a long chain fatty acid.

10. An electric blasting initiator having in combination an ignition assembly containing a bridge wire and a loose ignition mixture disposed about the bridge wire which comprises from about 64 to about 80% lead, from about 20 to about 36% selenium, and a minor amount of metal salt of a long chain fatty acid.

11. An electric blasting initiator having in combination an ignition assembly containing a bridge wire and a loose ignition mixture disposed about the bridge wire which comprises from about 64 to about 80% lead, from about 20 to about 36% selenium, and additive amounts of from about .2 to about 2% silicon, and from about .5 to about 2.0% of lead stearate.

12. A delay electric blasting initiator having in combination a delay fuse element and a loose ignition mixture in contact with the delay fuse element; said mixture comprising from about 64 to about 80% lead, from about 20 to about 36% selenium, and a minor amount of metal salt of a long chain fatty acid.

13. A delay electric blasting initiator having in combination a delay fuse element and a loose ignition mixture in contact with the delay fuse element; said mixture comprising from about 64 to about 80% lead, from about 20 to about 36% selenium, and additive amounts of from about .2 to about 2% silicon, and from about .5 to about 2.0% lead stearate.

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