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SODIUM CHLORATE COMPOSITIONS OF REDUCED FIRE HAZARD CONTAINING AN ALKALI METAL SILICATE FIRE RETARDANT

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U.S. Cl. 252—8.1 14 Claims

ABSTRACT OF THE DISCLOSURE

An alkali metal silicate alone or in combination with one or more alkali metal or ammonium-chromate, hydroxide, carbonate, sulfate, borate and phosphate when added to solutions of an alkali metal or ammonium chlorate in minor amounts will act as flame retardants for combustible organic material upon which the chlorate has been deposited. The function of these flame retardants when added to chlorate containing solutions does not detract from the function of the chlorate solution in electrochemical machining, milling and grinding operations or in agricultural applications.

This invention relates to compositions of matter containing an alkali metal or ammonium chlorate (preferably sodium chlorate), an alkali metal silicate and optionally other inorganic compounds. These compositions find utility in the field of *agricultural chemistry* as soil sterilizers, defoliants, and weed killers. These compositions also have utility as *electrolytes* for use in electrochemical machining and grinding operations. The compositions are especially useful because of their flame retardant properties.

Alkali metal and ammonium chlorates, especially sodium chlorate, are ideal electrolytes for use in electrochemical machining operations. The major problem attending their use resides in their tendency to rapidly oxidize combustible materials. The advantages and problems residing in the use of chlorates as the electrolyte in electrochemical machining operations are summarized in the article appearing in Metal Progress, March 1967, pp. 81–84. For example, when some of the chlorate containing electrolyte comes into contact with the clothing of the operator, or any combustible material near an electrochemical machining operation, the tendency to initiate fire is great after the wetted material has dried.

By electrochemical machining operations it is intended to include those operations by which a workpiece is machined, milled, or ground so that the metal is removed by an electrochemical process to produce shaped or curved structures. These operations also include the production of smooth flat surfaces and the formation of holes in a workpiece. The workpiece to be shaped functions as the anode in electrically conducting relationship with the cathode die through a suitable electrolyte. Metal is dissolved from the workpiece anode. Some electrolytes used in electrochemical machining are described in U.S. 2,798,846 to Comstock, issued July 9, 1957 as $NaNO_2$, Na_2CRO_4, KNO_2, K_2CrO_4, the amines of sodium nitrate, sodium and potassium dichromate, sodium and potassium chlorate and sodium and potassium chlorite. Essentially, the selection of the electrolyte is based upon its conducting properties, its tendency to attack the electrodes, its performance in electrochemical machining operations and its cost. Comstock mentions the rusting of a workpiece and its prevention through the use of a rust inhibiting agent as the electrolyte.

Sodium chlorate is an excellent electrolyte for electrochemical machining operations. Sodium chlorate solutions used as the electrolyte in electrochemical machining are typically aqueous solutions containing about 350 g./l $NaClO_3$. Solutions containing from about 300 to 400 grams per liter $NaClO_3$ are typical examples of efficient electrolytic solutions. The used electrolyte solutions, usually of pH above about 6 to 7, contain precipitated hydroxides of the metal removed from the workpiece. For example, where the workpiece contains iron, nickel or chromium, the corresponding iron, nickel or chromium hydroxides are formed.

In the electrochemical machining of chromium containing alloys, some soluble sodium chromate is introduced into the sodium chlorate electrolyte. The introduction of small amounts of sodium chromate into the electrolyte actually increases the fire hazard attending the action of chlorate on combustible organic material. Hence, any flame retardant additive will have to function in the presence of at least low concentrations of dissolved CrO_4^{-2} ions. It is also important that any additive must not change the characteristics of sodium chlorate in its operation as an electrolyte. However, it is most desirable that an additive both act as a flame retardant and improve the properties of sodium chlorate as an electrolyte.

In the field of agricultural chemistry, alkali metal chlorates have been used as defoliants (especially for cotton), weed killers, soil sterilizers, insecticides and as seed disinfectants. One of the major drawbacks to the use of chlorates as agricultural chemicals resides in the problem of its flammability when dried in contact with organic matter such as the workers' clothing. The discovery of additives such as an alkali metal silicate alone or in conjunction with a co-additive for the chlorate solutions used in agricultural applications obviates this objection to the use of chlorates and broadens the field for uses of chlorates at concentrations heretofore considered too dangerous for handling by the layman.

It is the object of this invention to develop compositions of matter containing a major proportion alkali metal chlorate in combination with one or more additives, the latter functioning as flame retarding agents when said compositions are deposited in a dry state upon combustible organic materials.

It is an additional object of this invention to provide compositions of matter containing a major proportion of alkali metal chlorate with minor proportions of one or more additives which will function as a flame retardant and as the electrolyte in electrochemical machining operations with the same degree of effectiveness as sodium chlorate alone.

DETAILED DESCRIPTION OF THE INVENTION

It has been discovered that an alkali metal silicate, when dissolved in a solution with an alkali metal or ammonium chlorate, will act as a flame retardant when the solution is dried on a combustible material. The ratio of SiO_2 to chlorate may vary from 1:4 to about 1:40 on a dry weight basis. The preferred ratio of Na_2SiO_3 to $NaClO_3$ is between 1:4 and 1:10 on a dry weight basis. In an electrolytic solution, this ratio represents, for a solution containing between about 300 to 400 grams per liter $NaClO_3$, from about 7–75 grams of SiO_2 (as a soluble silicate) per liter and preferably between about 15 to 50 grams SiO_2 per liter.

The preferred silicate additive for chlorate containing solutions employed as electrochemical machining or grinding electrolytes is sodium metasilicate (Na_2SiO_3) which may be added either as the anhydrous salt or as a hydrate such as the nona-hydrate ($Na_2SiO_3.9H_2O$).

Other silicates such as the disilicate ($Na_2Si_2O_5$) and tetrasilicate ($Na_2Si_4O_9$), commonly referred to as water glass may be employed as the fire retardant additive for various chlorate containing compositions. However, as an electrolyte in electrochemical machining and grinding operations sodium metasilicate is preferred to silicates of lower Na/Si ratios such as water glass because the tendency of the latter silicates is to deposit hydrous SiO_2 from solution in the presence of chlorate.

Co-additives which may be advantageously employed in conjunction with the silicate additive are alkali metal or ammonium chromates, carbonates hydroxides, phosphates, sulfates, and borates. These co-additives are effectively present in an amount between 10 and 80 grams per liter of solution in the use of chlorate-silicate solutions as the electrolyte for electrochemical machining and grinding operations. On a dry weight basis, the ratio of silicate, expressed as SiO_2, and independently the co-additive to chlorate may be 1:4–40, while a more preferred ratio is about 10–25 parts of sodium metasilicate to from about 4–10 parts of sodium metaborate for every 100 parts of sodium chlorate and the most preferred ratio is 2:1:16 sodium metasilicate to sodium metaborate to sodium chlorate. Exemplary mixtures containing sodium chromate as the co-additive are those containing on a dry weight basis a mixture of about 10–25 parts of sodium metasilicate and from about 10 to 20 parts of sodium chromate for every 100 parts of sodium chlorate. The most preferred mixture containing sodium chromate as the co-additive is 1:1:8 sodium metasilicate to sodium chromate to sodium chlorate.

The most preferred aqueous solutions of electrolyte for electrochemical machining operations are those containing from 300 to 400 grams sodium chlorate per liter and from 30 to 100 grams sodium metasilicate per liter; or 30 to 100 grams sodium metasilicate per liter in combination with from about 12–40 grams per liter sodium metaborate; or from about 30–100 grams per liter sodium metasilicate in combination with about 30–80 grams per liter sodium chromate.

Since an aqueous solution containing between about 300 to 400 grams per liter of sodium chlorate and up to about 100 grams per liter of sodium metasilicate is alkaline in pH, it is desirable to include an appropriate amount of NaOH whenever an acidic co-additive such as borax ($Na_2B_4O_7$), sodium pentaborate ($Na_2B_{10}O_{16}$) or Na_2HPO_4 is used. If NaOH is not employed in conjunction with acidic co-additives, the pH drop of the electrolyte solution causes hydrolysis of the silicate and precipitation of hydrous SiO_2.

The alkali metal silicate additives alone are very effective flame retardant additives for chlorate induced combustion of organic materials in many applications. However, a further factor which must be considered in evaluating the flammability of chlorate electrochemical machining or grinding electrolyte which has been dried on cloth, is the presence of trace amounts of chromate ion in the chlorate containing solution. Trace amounts of chromate, usually equivalent to 0.05 to 2 grams of hexavalent chromium per liter appear in the electrolyte used in the processing of chromium containing metals as the probable result of complete oxidation of the chromium to CrO_4^{-2} during the machining or grinding operation. These trace amounts of chromate serve to accelerate the combustion of organic material which has been wetted by the chlorate containing solution and dried. This acceleration is very pronounced when a cloth wetted with the chlorate containing solution is quite dry (e.g. under normal room conditions at 20 percent relative humidity). The accelerating effect of chromate on chlorate induced combustion is less pronounced when the organic material contains more moisture, as under normal room conditions at 60 percent relative humidity, but it remains a very important factor to be considered relative to the effectiveness of a flame retardant additive. The effect of trace chromate on chlorate induced combustion is clearly illustrated in Example 1 of this specification.

An additional problem in the determination of flame retardant properties of additives for chlorates resides in the fact that the combustion rate of a cloth impregnated with sodium chlorate and a prospective flame retardant is often dependent upon the size of the ignition source. A large flame may cause rapid burning while a small ignition source such as a match or the coal of a cigarette may cause slow combustion. A flame retardant additive which is effective with respect to common accidental ignition sources which may attend the personal habit of an operator of an electrochemical machining apparatus, such as a match flame or cigarette coal, may be considered adequate for the protection of that person. However, the degree of effectiveness for the same additive may be less in flame retardancy towards a large ignition source.

The alkali metal silicates are extremely effective flame retardants for chlorate induced combustion. In the presence of trace amounts of chromate ions, the effectiveness of an alkali metal silicate as a flame retardant is somewhat diminished although it is still adequate to provide the degree of protection needed for the machine operator. However, the introduction of a co-additive in conjunction with the silicate, will produce a silicate based additive which is more effective than silicate alone under the conditions of low humidity, the presence of trace chromate and a large ignition source. The silicate based additives are superior to most other additive systems tested.

In essence, in any application of solutions containing chlorate ions, conventional formulations applicable to the art may be supplemented with the silicate fire retardant of this invention with or without the addition or complementary fire retardant additives.

For example, in the field of electrochemical machining, it may be desirable to add minor amounts of other electrolytes to the sodium chlorate solution containing the fire retardant additives of this invention. Such supporting electrolytes may be NaCl, NaBr, NaF, $NaNO_3$, etc.

It is to be understood that whenever chromate is referred to in the specification as a co-additive, it is intended to include Na_2CrO_4, or sodium dichromate or chromic acid in the presence of sufficient NaOH to produce chromate in situ via the reaction:

$$\text{Chromic acid or } Na_2Cr_2O_7 + x\text{NaOH} \rightarrow Na_2CrO_4$$

The following Examples I–XVI represents specific embodiments of this invention. They represent applicable additive concentration levels which will produce the desired result. The minimum operable concentration of the flame retardant additives is desirable because excessive concentrations may cause inferior performance of the chlorate solution as electrolyte in an electrochemical machining or grinding operation.

To determine the effect of an alkali metal silicate with and without other additives as a flame retardant for organic materials impregnated with alkali metal or ammonium chlorate, the following experiments were conducted.

EXAMPLES I–XVI

The burning tests employed in the determination of the effectiveness of a given flame retardant additive were conducted as follows:

Strips of cotton twill 6 feet by 1.5 inch were soaked in the test solution, wrung out and dried under controlled condition of humidity. The cloth strips were then hung vertically and ignited at the bottom with a 4 inch gas flame (large ignition source) or a 0.5 inch gas flame (small source). The time required to burn (or char) a 52 inch section of cloth was determined. In its original state, without treatment, this standard cloth burns in 35 seconds. Hence, any additive which will prevent more rapid burning produced by the alkali metal or ammonium chlorate is an effective fire retardant. In each test, the cloth strip was loaded with about one gram of solution per gram of cloth. Each solution contained 400 grams sodium chlorate per liter. This concentration approximates the usua' concentration of chlorate used for electrochemical machining (3 pounds per gallon=359 grams per liter).

to the electrochemical reaction which may be considered oxidation of the iron in the workpiece to the ferrous or ferric state. A suspension of hydrous metal oxides was formed in the recirculating electrolyte and slowly settled

TABLE 1.—BURNING TIMES FOR COTTON TWILL STRIPS IMPREGNATED WITH $NaClO_3$+ADDITIVES

[Burning time=sec./52-inch section, 1½ inches wide]

Ex.	Solution composition, gms./liter: $NaClO_3$	Solution composition, gms./liter: Additive(s)	Drying of strip, percent rel. humidity, 25° C.	Ignition flame size	Burning time for strip, sec., when solution contained gms. Cr/liter (present as N_2aCrO_4) of: No Cr	0.05 Cr	0.1 Cr	0.5 Cr	1.0 Cr	2.0 Cr	Other Cr
1	400	No additive	20	Small	6.0	4.1	3.2	1.9	2.0	1.9	
2	400	No additive	52	do	12.6						
3	None	Water only	(1)	Large	36						
4	400	77.9 Na_2CrO_4	20	Small							25 Cr=40 sec.
5	400	77.9 Na_2CrO_4	20	Large							25 Cr=2.7 sec.
6	400	77.9 Na_2CrO_4	57	do							25 Cr=54 sec.
7	400	12 NaOH	20	Small	70		12.5			2.4	
8	400	12 NaOH	20	Large	19.0		9.1			2.2	
9	400	12 NaOH	56	do	360					177	
10	400	50.8 Na_2SiO_3 (=25 SiO_2)	20	Small	>300			115		40	
11	400	50.8 Na_2SiO_3 (=25 SiO_2)	20	Large	254	94	65	6.9		4.5	
12	400	77 Na_2SiO_3 (37.5 SiO_2)	20	Large			185				
13	400	50.8 Na_2SiO_3 plus 26.3 $NaBO_2$	20	Small	300						
14	400	50.8 Na_2SiO_3 plus 26.3 $NaBO_2$	20	Large	249	280	250	230		100	
15	400	50.8 Na_2SiO_3 plus 46.7 Na_2CrO_4	20	Small							15 Cr=50 sec.
16	400	50.8 Na_2SiO_3 plus 46.7 Na_2CrO_4	20	Large							15 Cr=38 sec.

[1] 20 and 55.

It is apparent from this data that the burning time of the original cloth (Example 3) is drastically reduced by chlorate and further reduced by chlorate in the presence of trace amounts of chromate (Examples 1 and 2).

Experiments presented in Examples 4–6 demonstrate the effects of low humidity and large ignition flame size in decreasing the burning time of the chlorate impregnated cloth in the presence of sodium chromate as a flame retardant additive. The same effects are illustrated in Examples 7–9, as well as the effect of trace amounts of chromate, for the flame retardant sodium hydroxide.

Experiments resulting in the data presented in Examples 10 and 12 illustrate the flame retardant effect of sodium metasilicate in the presence of trace amounts of chromate and at a low humidity for a small ignition source. The addition of both sodium metasilicate and sodium metaborate exemplified in Examples 13 and 14 demonstrates the higher degree of flame retardancy attending the use of a co-additive with the silicate.

Examples 15 and 16 demonstrate the flame retardant properties of another silicate based additive of this invention, specifically sodium metasilicate and sodium chromate.

The alkali metal or ammonium chromate, carbonate, hydroxide, phosphate, sulfate, borate co-additives for alkali metal silicate based flame retardant additives of this invention perform the same function and may be used in substantially the same amounts as illustrated for chromate and metaborate to achieve substantially the same results.

EXAMPLE XVII

The solution described in Examples 13 and 14 in the preceding table was charged to the reservoir of an electrochemical grinding machine. The grinding wheel (1 inch in width) was a conductive-bonded mixture of alumina and copper grains. The grinding wheel was made the cathode relative to the workpiece-anode. The workpiece (a 3 inch wide bar of 304 stainless steel) was fed into the wheel which was set to give a specified depth of cut. During the cutting operation, the electrolyte solution was pumped from the reservoir and injected between the grinding wheel and the workpiece. Used electrolyte drained back to the reservoir. Several cuts were made across the workpiece as slots 1 inch wide and 0.05 to 0.10 inch deep.

The feed rate of the workpiece into the grinding wheel was varied when necessary to maintain a light load on the grinding wheel drive motor. The power input to the drive motor was kept at about 10 percent of the load theoretically needed to cut the metal workpiece by abrasion alone. Therefore, practically all of the metal removal was due in the electrolyte reservoir to form a brownish sludge. For an 0.05 inch deep cut, the grinder drew 1500 emperes at 11 volts and the 3 inch long cut was completed in 80 seconds. For a depth of cut of 0.10 inch, 1900 amperes were drawn at 10 volts and a 3 inch cut required 140 seconds for completion. The ground sulface was smooth and there was no evidence of excessive overcutting. The burning time of cloth impregnated with the used electrolyte was approximately the same as that for the original solution.

The presence of sodium metasilicate and sodium metaborate had no deleterious effect on the performance of sodium chlorate as an extremely efficient electrolyte in the electrochemical grinding operation. Likewise the alkali metal based silicate flame retardant additives of this invention when employed in conjunction with chlorate as an electrochemical grinding or machining electrolyte present no deleterious effect in the actual grinding or machining operation while affording the advantage of flame retardancy to protect the operator and his clothing from accidental damage from fire induced by the chlorate.

The illustration of a specific electrolyte containing solution in conjunction with an electrochemical grinding operation is representative of the operation of all the disclosed compositions in grinding and machining operations.

Having disclosed the invention, it will be apparent to those skilled in the art that obvious modifications may be made. For example, in any of the disclosed combinations of additives for $NaClO_3$, the amount of silicate plus coadditive present may be increased without deleterious effects. The minimum amount of the flame retardant additive or additives is the critical factor to be considered in most applications because of possible deleterious effects that may impair the function of the chlorate as an electrochemical machining electrolyte. Therefore, the examples herein presented are intended to be illustrative of the inventive concept rather than limitations upon the actual scope of the contribution.

If higher or lower chlorate concentrations are desired in electrochemical machining or grinding operation, the relative proportion of silicate and co-additive may be employed.

What is claimed is:

1. A composition of matter comprising a member selected from the group consisting of an alkali metal chlorate, ammonium chlorate and mixtures thereof, and a flame retardant proportion of a member selected from the group consisting of an alkali metal silicate and hydrates thereof, in which the silicate, expressed as SiO_2, to chlorate weight ratio is between about 1:4 to 1:40.

2. The composition of claim 1 in which sodium metasilicate and sodium chlorate appear in the weight ratio of about 1:4 to 1:10.

3. A composition of matter comprising a member selected from the group consisting of an alkali metal chlorate, ammonium chlorate and mixtures thereof; a flame retarding proportion of a member selected from the group consisting of an alkali metal silicate and hydrates thereof; and a flame retarding proportion of a co-additive selected from the group consisting of an alkali metal chromate, borate, carbonate, phosphate, sulfate, hydroxide, ammonium analogs thereof, hydrates thereof and mixtures thereof, in which the silicate, expressed as SiO_2, co-additive and chlorate are in the weight ratio of 1:1:4–40.

4. The composition of claim 3 comprising about 10–25 parts of sodium metasilicate, and about 4–10 parts of sodium metaborate to each 100 parts of sodium chlorate.

5. The composition of claim 3 in which the weight ratio of sodium metasilicate to sodium metaborate to sodium chlorate is about 2:1:16.

6. The composition of claim 3 comprising about 10–25 parts of sodium metasilicate and about 10–20 parts of sodium chromate to each 100 parts of sodium chlorate.

7. The composition of claim 3 in which the weight ratio of sodium metasilicate to sodium chromate to sodium chlorate is about 1:1:8.

8. An aqueous solution of an electrolyte comprising from about 300 to about 400 grams per liter of a member selected from the group consisting of an alkali metal chlorate, ammonium chlorate and mixtures thereof; about 7 to about 75 grams per liter of an alkali metal silicate, expressed as SiO_2; and from 10 to about 80 grams per liter of a co-additive selected from the group consisting of an alkali metal chromate, borate, carbonate, phosphate, sulfate, hydroxide, the ammonium analogs thereof and mixtures thereof.

9. The solution of claim 8 in which the chlorate is sodium chlorate, the silicate is sodium metasilicate and the co-additive is sodium metaborate.

10. The solution of claim 9 which contains from about 30–100 grams per liter of sodium metasilicate and from about 12–40 grams per liter of co-additive sodium metaborate.

11. The solution of claim 8 in which the chlorate is sodium chlorate, the silicate is sodium metasilicate and the co-additive is sodium chromate.

12. The solution of claim 11 which contains from about 30–100 grams per liter of sodium metasilicate and from about 30–80 grams per liter of co-additive sodium chromate.

13. The solution of claim 8 in which the chlorate is sodium chlorate, the silicate is sodium metasilicate appearing in from about 30 to 100 grams per liter and the amount of co-additive present is zero.

14. A method of retarding chlorate induced combustion of organic material which comprises incorporating into aqueous solutions containing the chlorate ion, a flame retardant proportion of an alkali metal silicate and a flame retardant amount of a co-additive selected from the group consisting of an alkali metal chromate, carbonate, borate, phosphate, sulfate, hydroxide, ammonium analogs thereof and mixtures thereof, in which the silicate, expressed as SiO_2, co-additive and chlorate are in the weight ratio of 1:1:4–40.

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CERTIFICATE OF CORRECTION

Patent No. 3,645,895 Dated February 29, 1972

Inventor(s) John A. Peterson and Albert H. Ross

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 12, "carbonates" should read ---carbonates,---. Column 4, line 33, "addition or" should read ---addition of---. Column 6, line 26, "emperes" should read ---amperes---; line 30, "sulface" should read ---surface---.

Signed and sealed this 18th day of July 1972.

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