Sept. 29, 1959 J. D. NICKERSON 2,906,632

OXIDATION RESISTANT ARTICLES

Filed Sept. 10, 1957 3 Sheets-Sheet 1

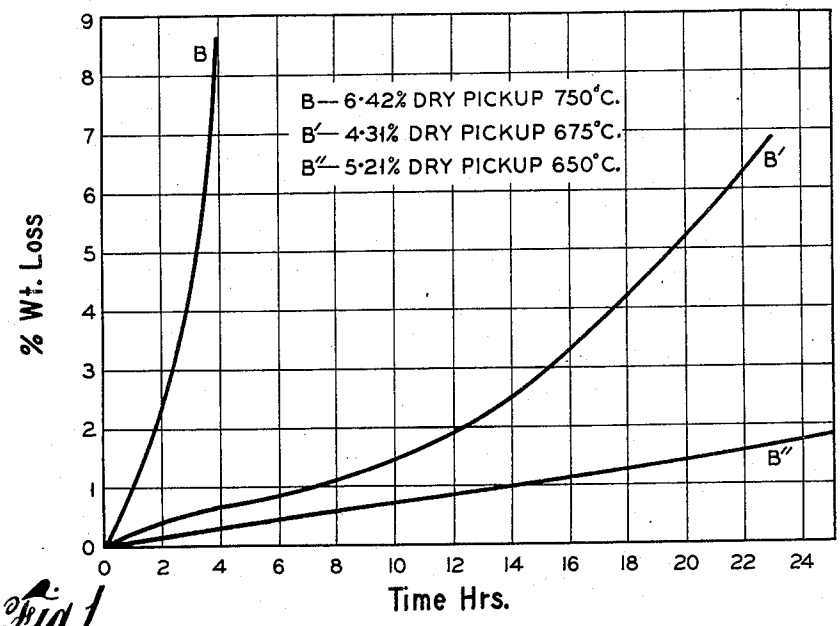



Fig. 1.

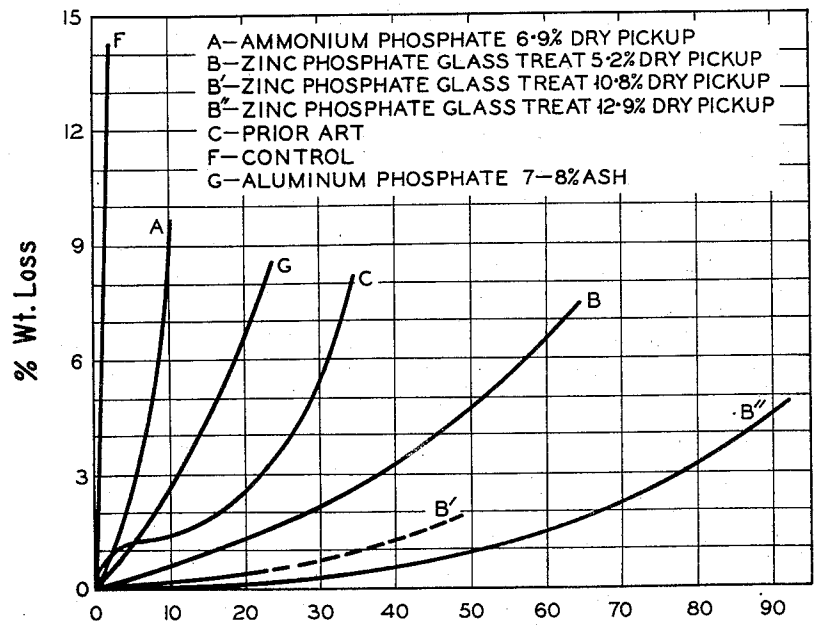



Fig. 2.

INVENTOR.
J. DAVID NICKERSON
BY
John F. Hohmann
ATTORNEY

OXIDATION RESISTANT ARTICLES

Filed Sept. 10, 1957 3 Sheets-Sheet 2

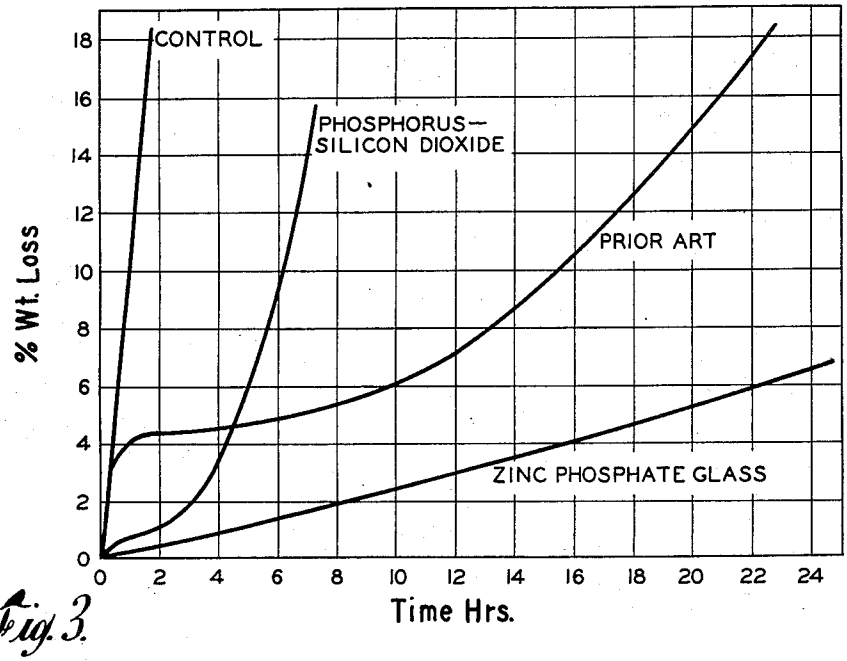



Fig. 3.

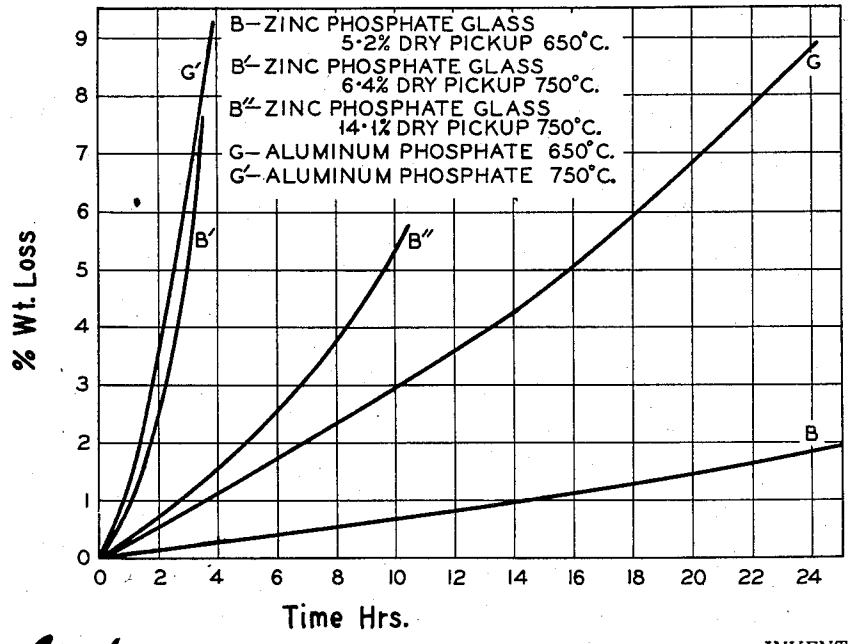



Fig. 4.

INVENTOR.
J. DAVID NICKERSON
BY
John F. Hohmann
ATTORNEY

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# OXIDATION RESISTANT ARTICLES

Filed Sept. 10, 1957 3 Sheets-Sheet 3

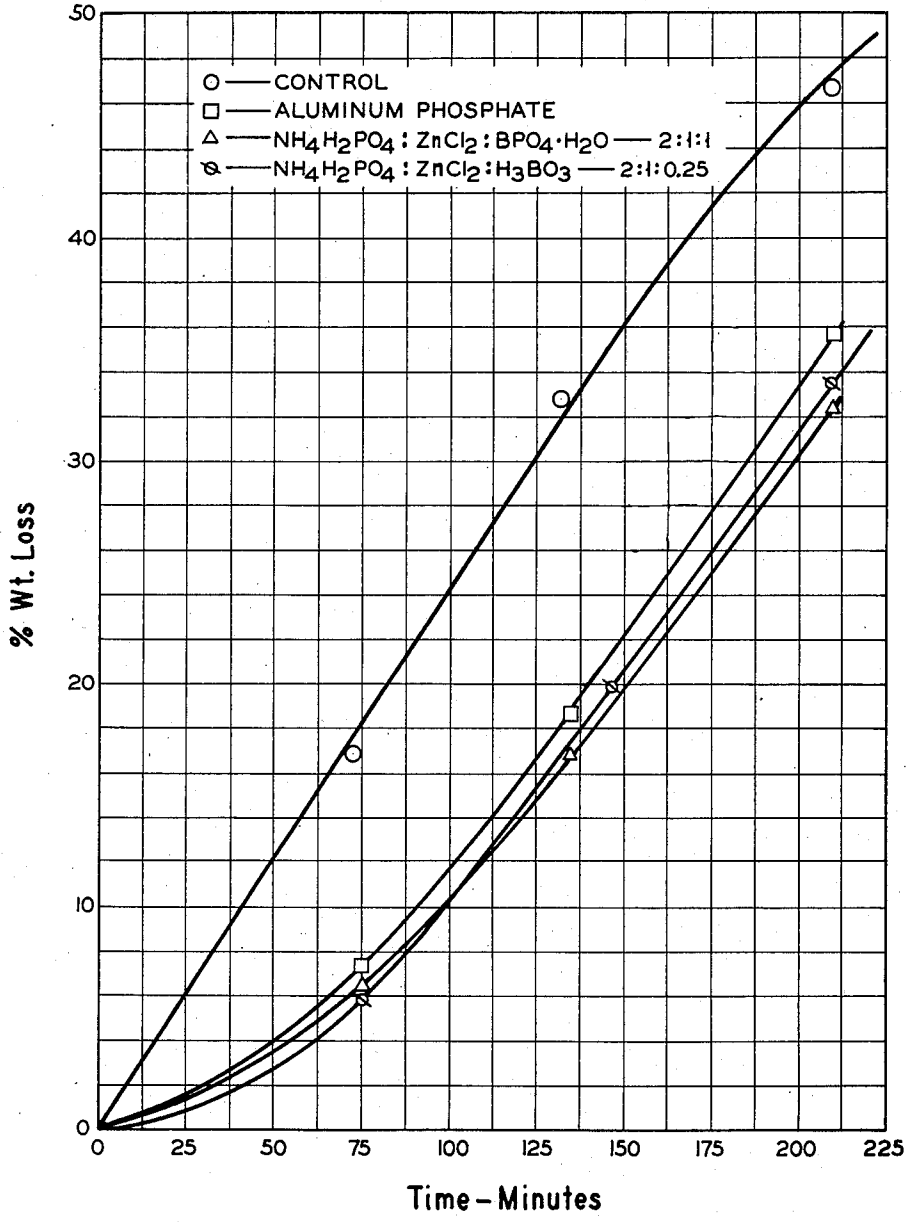



Fig. 5.

INVENTOR.
J. DAVID NICKERSON
BY
John F. Hohmann
ATTORNEY

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2,906,632

# OXIDATION RESISTANT ARTICLES

John D. Nickerson, Lakeland, Fla., assignor to Union Carbide Corporation, a corporation of New York

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3 Claims. (Cl. 106—56)

This invention relates to methods for rendering carbonaceous articles oxidation resistant. More specifically, the invention relates to methods of providing zinc phosphate compounds in carbon and graphite bodies to render such bodies resistant to oxidation at temperatures upwards of 600° C.

Because of the frequent uses made of carbon and graphite bodies in furnace linings and other high temperature applications in the presence of materials which themselves exert an oxidizing influence on their surroundings, it is necessary that such articles possess resistance to oxidation at high temperature.

A great many methods have been devised to render carbon articles oxidation resistant, but their success has not been such that the problem no longer confronts industry. Among the various additives used as oxidation retardants have been diverse phosphorus-containing compounds. Thus prior art has amply taught that phosphoric acid tends to increase the oxidation resistance of carbonaceous bodies. It has been found also that many organic phosphates as well as the phosphate salts of sodium, aluminum, calcium, potassium and magnesium are effective oxidation reducing additives. In general, however, methods of protection, depending upon the above-mentioned additives, are neither exceptionally effective nor long lasting in effect.

Bearing in mind the above outlined limitations of prior art attempts to render carbon and graphite bodies oxidation resistant, the primary object of the present invention is to provide improved methods for rendering such articles oxidation resistant at temperatures up to 950° C.

An equally important object of the invention is to provide articles composed of carbon and graphite, which possess improved resistance to oxidizing conditions at temperatures up to 950° C.

A further object of the invention is to provide zinc phosphate compounds in carbon parts, which compounds serve to maintain the original dimensions of such parts despite loss of weight by the same.

These and other objects and advantages of the invention will become apparent as the description thereof proceeds, particularly when taken in connection with the accompanying drawing in which:

Fig. 1 is a graphical representation relating the effects of temperature on the oxidation rates of samples treated in accordance with the method of the invention; and

Figs. 2, 3, 4, and 5 are graphical representations comparing the oxidation rates of samples treated following the method of the invention with those of samples treated with various prior art oxidation retardants.

The foregoing and related objects of the invention are attained by providing in carbon and graphite articles a composition consisting of a zinc phosphate compound or glass. The reagents required to form the zinc phosphate compound may be introduced into formed bodies by soaking or impregnation procedures, or may be incorporated, in their simple or combined form, in the "green" carbon mix.

The effective product of the composition is a very viscous liquid, which wets unoxidized carbon surfaces, and spreads through the carbon matrix to provide a barrier between the carbon and the surrounding atmosphere. This barrier provides long lasting and efficient oxidation protection at temperatures ranging from 500° C. to 950° C. In the practice of the invention, articles, the protection of which is desired, may be pre-heated to form a phosphate glass, or the glass may be allowed to form during service.



Best results are obtained in the practice of the invention when the weight ratios of forming agents; namely, ammonium phosphate, zinc chloride and boric acid are in the range of 4:1:0 and 2:2:0.25. The boron constituent may be omitted to give compositions about 20 percent superior to those given by compositions containing boron at temperatures of 725° C. to 750° C. At 675° C., however, such a composition will be about 10 percent less effective than when boron is present. Above 750° C., the differences in oxidation rates between the two are not significant. In effect, by varying the ratio of constituents and other features of the present invention, it is possible to obtain greater protection at a given temperature than at other temperatures above or below the given value, as will be disclosed more fully hereinafter.

In one embodiment of the invention, a shaped or amorphous carbon or graphite body is treated with an aqueous acid solution containing zinc phosphate-forming agents present in an amount ranging from 20 percent to 45 percent by weight. Depending upon the type of carbon or graphite stock involved, and the amount of retardant pick-up desired, the articles may be dipped in the solution or vacuum impregnated. Multiple treatments provide additional pick-up to desired higher levels. Treated articles may be dried at 110° C. or at room temperature, if time permits. A slow drying procedure is preferred because of the tendency of treated stock to "sweat" when rapidly heated.

Agents suitable for the practice of the invention include zinc halides, preferably zinc chloride, and at least one phosphorus-containing agent from the group consisting of the oxy acids of phosphors, ammonium salts of phosphorus such as monobasic ammonium phosphate, and boro-phosphoric acid ($BPO_4.H_2O$). Alternatively, boric acid may be used with the above compounds. In the preferred embodiment of the invention, best results are obtained when monobasic ammonium phosphate, zinc chloride and boric acid are used in the molar ratio 3:1:0.25. These constituents are dissolved in the order: boric acid; ammonium phosphate; and zinc chloride; in a 1.5 percent solution hydrochloric acid, employing great care to insure that each individual constituent is entirely dissolved prior to the addition of the next. The solution is kept acid to prevent the precipitation of zinc phosphate. Preferably about 0.1 percent of a commercially available wetting agent should be added to the solution to speed the penetration thereof into carbon or graphite pores. In a specific example of the invention a 30 percent solution by weight containing the above weight ratio of the agents was admitted to a previously evacuated vessel containing a number of 1 inch x 1 inch x ½ inch samples of graphite. Four to 5 percent dry pick-up of solution was observed after one impregnation, and it was possible to obtain an 8 to 9 percent pick-up without forming a white coating on the articles. In another example of the invention, 20 inch x 72 inch thermic electrodes were dipped for 30 seconds in the same solution as above indicated, and an 0.5 percent dry pick-up was observed. In each case the dry samples exhibited no hygroscopicity.

Table I compares the performance of treated and untreated samples at 500° C.

TABLE I

| Treatment | Time (hrs.) | Percent weight loss at indicated time [3] |
|---|---|---|
| Control | 6 | 5.01 |
| | 12 | 10.4 |
| | 18 | 15.5 |
| | 24 | 21.0 |
| Uncured,[1] 10% dry impregnated pickup | 0 | 0 |
| | 6 | 0.15 |
| | 12 | 0.18 |
| | 18 | 0.23 |
| | 24 | 0.27 |
| Cured,[2] 15% dry impregnated pickup | 6 | 0.13 |
| | 12 | 0.21 |
| | 18 | 0.27 |
| | 24 | 0.35 |

[1] "Uncured" refers to the series of operations of impregnating with the solution, drying at 100° C. and then oxidizing at 500° C.
[2] "Cured" refers to the series of operations if impregnating, drying at 100° C., heating under nitrogen to 700° C. and then oxidizing at 500° C.
[3] Where large initial weight losses occurred due to volatile components of the treat, these weights have been subtracted from the total loss to give the oxidation losses listed above.

In Table II below are shown typical oxidation results obtained with graphite samples impregnated with solutions containing indicated weight ratios of reagents, mono-basic ammonium phosphate, zinc chloride and boric acid, respectively.

TABLE II

*Oxidation at 675° C.*

| Sample No. | Ratio of reagents | Percent dry pick-up | Percent loss after— | |
|---|---|---|---|---|
| | | | 2 hours | 19 hours |
| 1 | 2:2.0:0.25 | 5.6 | 2.4 | (30) |
| 2 | 2:1.0:0.25 | 4.3 | 0.25 | 1.2 |
| 3 | 2:1.0:0.00 | 3.8 | 0.56 | 5.3 |

In a further embodiment of the invention zinc-phosphate-forming agents were added directly to the "green" carbonaceous mix. In typical examples of this embodiment, zinc chloride and boro-phosphoric acid were added in amounts from 4 to 20 parts per 100 in the aggregate, to green mixes formed by commingling 75 percent by weight of carbon flour, 25 percent by weight of coke, and 34 parts per 100 of coal tar pitch melting at around 120° C. Table III below shows the results obtained with baked carbon stock containing the indicated amounts of zinc phosphate compound.

TABLE III

*Oxidation temperature 725° C.*

| Quantity of additive in p.p.h. | | | Percent oxidation loss after— | | |
|---|---|---|---|---|---|
| $ZnCl_2$ | $BPO_4.H_2O$ | $H_3BO_3$ | 1 hr. | 2 hrs. | 4 hrs. |
| 2 | 2 | ----- | 2.5 | 14.5 | 33 |
| 6 | 6 | ----- | 1.8 | 9.6 | 18 |
| 2 | 2 | 6 | 1.7 | 9.2 | 14 |
| 6 | 14 | ----- | 1.6 | 8.1 | 16 |
| Control | ------ | ----- | 2.3 | 17 | 31.1 |

In another variant of the invention, reaction products formed at high temperatures by various zinc phosphate-forming agents were added to the "green" carbon mix. Table IV below shows the results of adding the reaction product formed at 500° C. by mono-basic ammonium phosphate, zinc chloride and boric acid to a "green" mix consisting of 75 percent carbon flour, 25 percent coke flour, and 34 parts per 100 of coal tar pitch binder. The reaction product was added in a crushed form such that it passed through a 100 mesh screen.



TABLE IV

*Oxidation temperature 600° C.*

| P.p.h. residue added | Percent loss after— | | | | |
|---|---|---|---|---|---|
| | ¼ hr. | 1 hr. | 2 hrs. | 5 hrs. | 19 hrs. |
| 29 | 3.3 | 8.1 | 11.0 | 14.2 | 31.1 |
| 5 | 2.0 | 5.9 | 10.6 | 21.9 | ---------- |
| 0 | 2.4 | 8.4 | 17.1 | 34.1 | ---------- |

A still further modification of the invention is based on the discovery that zinc chloride and ammonium phosphate, or zinc chloride and boro-phosphoric acid provide excellent oxidation protection if the treated samples are pre-heated, preferably in a non-oxidizing atmosphere, to 800° C. to 900° C., respectively. This pre-heating is required to promote reaction and form a protecting medium of suitable characteristics to permeate the matrix.

The exact mechanism whereby the beneficial effects of the invention are attained is not known exactly. However, it has been noted that the formation of the protective glass medium takes place in three discrete steps:

(1) Between 200° C. and 500° C., the reagents react with the evolution of ammonium chloride and hydrogen chloride. This reaction is accompanied by a spreading of the reactants over the exposed surface of the carbon or graphite article.

(2) Between 500° C. and 700° C., the reaction product changes to a very viscous liquid which wets the carbon and forms a barrier against oxidation. Upon cooling, the mass is crystalline, and the phosphate can be identified by diffraction techniques. The type of phosphate formed naturally depends upon the relative proportions of reactants.

(3) Above 650° C. to 700° C., a reaction of the zinc phosphate compound occurs such that upon cooling, the mass resembles a glass. It has been observed that at 650° C. the very viscous zinc phosphate glass causes a secondary bonding to the treated material. Even after 50 per cent weight loss of the carbon or graphite sample, the original dimensions of the unoxidized sample are not effected. Through its wetting action and very viscous nature at that temperature the glass serves as a bond between what normally would have become a discontinuous carbon phase at that weight loss level. This bond serves as a means of maintaining the dimensions of treated parts, and of prolonging stock life in the case of molds and chill trays.

Referring now to the drawing, Figure 1 shows the effect of temperature upon the oxidation rate of samples which have been impregnated to the dry pickups indicated with a 2:1:0.25 ammonium phosphate, zinc chloride and boric acid solution. The graph shows that there is approximately a two-fold increase in oxidation rate upon going from 650° C. to 675° C. Also indicated is the fact that the oxidation rate of stock treated in the manner of the invention at 750° C. is comparable to the control rate at 650° C.

In Figure 2 are given comparisons between the glass of the invention and other oxidation retardants as listed. The curve which is labeled "C" is a sample of stock impregnated with calcium phosphate and/or magnesium phosphate. The discerning feature is the change in rate of the various plots. The method of the invention treat is observed to be more enduring than other methods, and its advantage over ammonium phosphate is very apparent. Thus, it can be seen that the method of the invention protection is more enduring and more effective than the protection obtained by other procedures.

Figure 3 gives a further comparison between various treats and the present method at 675° C.

Figure 4 is a comparison between aluminum phosphate and the present additives at 650° C. and 750° C.

for equivalent quantities of ash, G' and B'' should be compared at 750° C.

In Figure 5 are shown the results of oxidation tests at 900–925° C. run on samples impregnated with the 2:1:0.25 composition as compared to a sample of aluminum phosphate and a sample in which boro-phosphoric acid has been substituted for boric acid. The samples of treated stock in all cases exhibit lower initial rates of oxidation than does the control. However, after seventy-five minutes, the rate of treated stock raises to that of the control.

What is claimed is:

1. An oxidation resistant article consisting of a carbonaceous matrix selected from the group consisting of carbon and graphite, having from about 4 percent to about 20 percent by weight thereof of a zinc phosphate composition comprising essentially ammonium phosphate, zinc chloride and boric acid in the ratios of between 4:1:0 and 2:2:0.25.

2. A process for producing oxidation resistant carbonaceous articles consisting in placing from about 4 to about 20 percent by weight of a zinc phosphate composition in the pores of said articles, said composition consisting essentially of at least one phosphorus-containing compound selected from the group consisting of the oxy acids of phosphorus and the ammonium salts of phosphorus, a zinc halide, and boric acid, the rate ratio of said compounds being between 2:1:0 and 2:2:0.25.



3. An oxidation-resistant article consisting of a carbonaceous matrix selected from the group consisting of graphite and carbon, and having therein from about 4 percent to about 20 percent by weight of a composition consisting essentially of a phosphorus-containing agent selected from the group consisting of the oxy acids of phosphorus and the ammonium salts of phosphorus, together with a zinc halide and a boric acid, the weight ratios of said materials ranging between 2:1:0 and 2:2:0.25.

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