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Production of Benzoate Color Agents

by K.L. and B.J. Kosanke

The use of copper(II) benzoate as a blue color agent was discussed by Bleser.[1] In large part, the endorsement for its use is based on its ability to serve as both color agent (copper) and fuel (benzoate). There is something to be said for this approach. For example, consider a color agent such as copper(II) carbonate ($CuCO_3$); it is only the copper that is useful in producing color. (See Reference 2 for a more complete description of colored flame production.) What is more, energy is required to free copper from its carbonate ion. Consequently, the flame temperature is lowered, which in turn results in less colored light output. It would be preferred if the copper could be made available without having to pay the full energy cost of freeing it from the carbonate ion. One way to do this is to chemically combine copper with a fuel such as the benzoate ion. Then, when the fuel is consumed, copper will be left over and ready to make the blue color-generating molecule, copper monochloride (CuCl). Because copper benzoate is not commonly available, Bleser described one way to produce it. There is, however, another way to produce copper benzoate. This process is a little more complicated, but the same basic process can also be used to make many other interesting pyrochemicals, only one class of which are benzoates.

When an acid is mixed with a carbonate or bicarbonate in the presence of water, the resulting chemical reaction produces carbon dioxide [soda water gas, CO_2] and water [H_2O], plus the metal salt of the acid. One familiar example of the process is that observed when vinegar [a dilute solution of acetic acid, $HC_2H_3O_2$] is added to baking soda [sodium bicarbonate, $NaHCO_3$] producing the sodium salt of acetic acid [sodium acetate, $Na(C_2H_3O_2)$] with much frothing and fizzing as gaseous carbon dioxide escapes. The reaction is described in the following chemical equation:

$$HC_2H_3O_{2(aq)} + NaHCO_{3(s)} \rightarrow Na(C_2H_3O_2)_{(aq)} + H_2O_{(l)} + CO_{2(g)} \qquad (1)$$

The physical states of the substances are indicated by (s) for solid, (l) for liquid, (g) for gas, and (aq) for aqueous or dissolved in water.

In a manner similar to Equation 1, the reaction of a benzoic acid solution [$HC_7H_5O_2$] with copper(II) carbonate [$CuCO_3$] yields the color agent and fuel, copper(II) benzoate [$Cu(C_7H_50_2)_2$]. This is shown in Equation 2.

$$2\ HC_7H_5O_{2(aq)} + CuCO_{3(s)} \rightarrow Cu(C_7H_5O_2)_{2(s)} + H_2O_{(1)} + CO_{2(g)} \qquad (2)$$

Since benzoic acid comes as a solid (much like boric acid or stearic acid, which are more familiar to pyrotechnists), it must be dissolved before it will react in this way. In addition, because benzoic acid is not very soluble, the water must be heated to encourage more of the benzoic acid to go into solution and thus allow the reaction to proceed. After the reaction is completed, recovery of the benzoate is easy; the carbon dioxide by-product is lost to the atmosphere, and the water by-product is removed by drying.

In Equation 2, if the copper(II) carbonate is replaced with strontium carbonate, strontium benzoate can be produced. Similarly, the use of barium carbonate produces barium benzoate, and calcium carbonate produces calcium benzoate.

Following is a simple procedure to produce these unusual, but potentially effective color agents. See Table 1.

Table 1. Production or Benzoate Color Agents.

Reactant	Parts by Weight[(a)]	Product	Parts by Weight[(b)]
Benzoic acid	12		
Metal Carbonates:		Metal Benzoates:	
Barium carbonate	11	Barium benzoate	19
Calcium carbonate	5.5	Calcium benzoate	14
Copper(II) carbonate[(c)]	6	Copper(II) benzoate	15
Strontium carbonate	8	Strontium benzoate	17

Notes:

(a) These amounts include a slight excess of carbonate to assure the complete reaction of the benzoic acid.

(b) These are the theoretical amounts that can be produced. In actual practice, the amount produced depends on the exact procedure followed. However, generally only about 80% of these amounts will be recovered for use.

(c) Note that copper(II) carbonate as used in fireworks is more accurately basic copper(II) carbonate, which is $CuCO_3 \cdot Cu(OH)_2$. The weight shown in the table correctly reflects this fact.

Procedure

A) Place no more than about 50 parts by weight of water into a glass container. (It is desirable to use a minimum amount of water. With experience, it will often be found that less water can be used.) The container should be generously oversized so that when the reaction proceeds with the evolution of carbon dioxide, and the mixture froths-up, none will be spilled.

B) Using the information in Table 1, weigh the ingredients to make the desired metal benzoate; for example, to make barium benzoate, weigh out 12 parts benzoic acid and 11 parts barium carbonate.

C) Add all of the benzoic acid and about ¼ of the metal carbonate to the water and stir. The mixture may be a fairly thick slurry.

D) Begin warming the mixture until bubbles of carbon dioxide are observed. Stir the mixture to help break-up the froth of gas bubbles being produced.

E) When the production of CO_2 is essentially complete, add another increment of the carbonate. Repeat until all the remaining carbonate has been added.

F) Once all of the carbonate has been added and no more bubbling is observed, heat a little further and continue to stir to insure that the reaction is complete.

G) Before proceeding to the next step it is useful (and sometimes, important, depending on the solubility of the product benzoate) to boil off most of the excess water. Heat the mixture slowly until no significant amount of water remains visible. (This will assure a good yield of product even for benzoates that are highly soluble in water.)

H) Allow the mixture to cool and then dump the product material (the metal benzoate) on a mat of paper towels to absorb most of the remaining water.

I) Allow the material to air dry for several days or place in an oven, at 225 °F, with air circulation until dry.

J) Pass the dried material through a screen to break up any lumps.

Cautions

Essentially all copper, strontium and barium salts are somewhat toxic. For example, the J.T. Baker Saf–T–Data health and contact ratings for these metal carbonates range from 1 (slight) to 2 (moderate). Because of the increased solubility of benzoates, their ratings will probably all be at least 2 (moderate). [As a point of reference, note that barium nitrate has a health rating of 3 (severe).] Accordingly, some degree of caution is appropriate when working with these materials. Certainly any glassware used to make these benzoates, and any oven used to dry them, should not be used to prepare food.

The authors have produced metal benzoates using this method, but have not developed formulations for them, nor have they tested the sensitivity of any formulation using them.

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References

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