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SODIUM FLUOCHROMATE AND THE PROCESS FOR PREPARING THE SAME

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This invention relates to a new chromium compound, and is more particularly concerned with an air-stable and soluble divalent chromium salt useful in metal deposition.

Certain metal plating operations require the use of aqueous solutions containing chromous ions. Replacement of the divalent chromium as it is used up is necessary in order to maintain the activity of a plating bath. For this and other purposes it is desirable to have a stable chromium salt which can be added directly to aqueous baths to form chromous ions in solution.

It is an object of this invention to provide a new salt of divalent chromium. Another object is to provide such a salt which is stable in air and ionizes in aqueous solution to furnish chromous ions. A further object is to provide new plating baths and processes for plating metal using solutions of this divalent chromium salt. Other objects will become apparent from the specification and claims.

In accordance with this invention it has been found that a novel chromium compound, sodium fluochromate (II), Na_2CrF_4, is formed by reacting sodium fluoride with a soluble divalent chromium compound in aqueous solution. Sodium fluochromate (II) crystallizes in the form of needles which mat together much like asbestos and are pale to strong clear blue depending on the particle size. It is not strongly ferromagnetic.

An X-ray powder diffraction pattern of a sample 94–98% pure showed a characteristic pattern of lines with 4.86, 2.81, and 2.76 A. as the strongest lines. The complete pattern is described in the following table, where d is the spacing in Angstrom units and I/I_0 is the relative intensity (S=strong; M=medium; F=faint; V=very faint).

d	I/I_0	d	I/I_0	h	I/I_0
4.86	S	2.31	V	1.85	V
4.74	V	2.21	V	1.75	M
3.63	V	2.19	M	1.67	M
2.81	S	2.15	M	1.62	M
2.76	M	2.10	M	1.60	M
2.69	M	2.05	M	1.59	M
2.50	V	2.00	M	1.41	M
2.42	V	1.94	F	1.38	M
2.38	F	1.92	M	1.35	M

The compound appears to be stable indefinitely in air under normal conditions. Heating to 180° C. in air for one hour produces less than 0.2% change in weight and no change in titratable chromous ion content. Its stability, together with its appreciable solubility, make it a very convenient source of chromous ions.

The solubility of sodium fluochromate (II) appears to depend upon the concentrations of Na^+, Cr^{++} and F^- in solution, the indicated molal solubility product being of the order of

$$[Na^+]^2\,[Cr^{++}]\,[F^-]^4=10^{-3}\text{ to }10^{-4}$$

However, in hot deoxygenated water the compound does not dissolve, but solwly evolves hydrogen. It behaves in chemical reactions like a loose complex of Na^+, Cr^{++} and F^-. It reacts with strong acids to form solutions which exhibit the characteristic clear blue of

aqueous chromous ion. It dissolves, forming strongly colored chromium (II) complexes, in formate, glycolate, lactate and oxalate buffer solutions. Water-soluble chromous complexes are also formed with ammonia, glycine, ethylene diamine and ethylenediaminetatraacetic acid.

Chromous acetate, benzoate, borate and phosphate are formed as insoluble colored precipitates by reaction of Na_2CrF_4 with the corresponding buffers. There is no evidence that fluoride ion accompanies chromous ion in these reactions, which are all quite rapid. Sodium fluochromate (II) shows strong reducing properties due to the available chromous ion as, for example, in reduction of Ag^+, Cu^{++}, Ni^{++} and Sb^{+++} to metals.

A convenient method for preparing sodium fluochromate (II) is illustrated by the following example, in which parts are by weight:

Example 1

The procedure is carried out under nitrogen, and deoxygenated water is used, to avoid oxidizing Cr^{++} to Cr^{+++} or higher. Chromous sulfamate is prepared by reacting 20.0 parts of pure chromium powder with 40.0 parts of sulfamic acid in 200 parts of water. The reaction temperature is slowly raised from room temperature to 90° C. After an induction period the chromium reacts until the sulfamic acid is substantially used up according to the reaction:

$$Cr+2NH_2SO_3H\rightarrow H_2+Cr(NH_2SO_3)_2$$

The resulting solution, which is a strong bright blue, is filtered to remove unreacted chromium metal. An extra 200 parts of water is used for rinsing the unreacted chromium and combined with the initial filtrate.

The solution of chromous sulfamate is mixed with a suspension of 35.0 parts of sodium fluoride in 200 parts of water in a stirred flask. The stirred mixture is heated to about 80°–100° C. and then allowed to cool. Sodium fluochromate (II) is formed according to the following reaction and precipitates:

$$Cr(NH_2SO_3)_2+4NaF\rightarrow Na_2CrF_4+2NaSO_3NH_2$$

Usually a dense precipitate forms first, followed by growth of a very bulky precipitate which again becomes more dense. The precipitate is filtered and washed, first with 50% methanol (in which $NaSO_3NH_2$ and any excess NaF are appreciably soluble), and then with methanol. Air drying of the precipitate is satisfactory, but vaccum drying can be used. There is obtained 27.9 parts of Na_2CrF_4, which corresponds to a yield of 77% on NaF, 78% on sulfamic acid and about 75% on reacted chromium. Precipitation is incomplete at the stoichiometric ratio used in this example, but complete precipitation of Na_2CrF_4 is apparently achieved in other cases by use of an excess of sodium fluoride.

Analysis	Found	Calculated for Na_2CrF_4
Na	27.81	26.4
F	43.09	43.7
Cr (total)	29.50	29.9
Cr (divalent)	28.61	29.9

The sodium fluorchromate (II) is readily crystallized in the form of blue needles about 0.4 mm. in length which mat together. The new salt is useful for forming chromium (II) complexes in baths used in corrosion-protective coating or electrolytic plating processes. Such use is illustrated by the following example:

Example 2

Sodium fluochromate (II) dissolves in ammonical ammonium chloride solution to form a deep blue ammonia-complexed chromous ion solution. Nickel chloride also dissolves in this solution to form a complex. The mixture of complexes reacts at 90°–100° C. with deposition of a corrosion-protective coating. The reaction can be used to form coatings or extremely fine metallic precipitates. For corrosion-preventive coating, nickel-boron flashed copper (0.01–0.02 mg. Ni-B/cm.^{2}) is immersed in an aqueous solution of the following components and maintained at 90°–100° C. for 15 minutes:

	Molal
Maleic acid	0.75
Ammonium hydroxide	5.5
Boric acid	1.5
Nickel chloride	0.037
Sodium hypophosphite	0.17
Sodium fluochromate (II)	0.052

A bright coating forms weighing 0.1 mg./cm.^{2}. When tested for corrosion resistance in a humid atmosphere of sulfur dioxide at room temperature, the time to destruction of the coating in this highly accelerated corrosion test was 305 minutes. For comparison, the time to destruction for a similar weight of nickel-boron coating, or nickel coating prepared by other methods, is only about 15 minutes.

The activity of the bath used in the above example is maintained by periodic addition of sodium fluochromate (II).

Since many different embodiments of the invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited by the specific illustrations except to the extent defined in the following claims.

I claim:

1. Sodium fluochromate (II).

2. The crystalline divalent chromium salt of substantially the formula, Na_2CrF_4, characterized by high stability in air and appreciable solubility in water.

3. The process for preparing sodium fluochromate (II) which comprises heating an aqueous solution of sodium fluoride and chromous sulfamate to about 80°–100° C., cooling the solution to precipitate sodium fluochromate (II), and separating the precipitated sodium fluochromate (II) from the reaction mixture.

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