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### A Study of Aldehyde Derivatives of Metallic Sulfamates.

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**A STUDY OF ALDEHYDE DERIVATIVES OF METALLIC SULFAMATES**

being

A thesis presented to the Graduate Faculty  
of the Fort Hays Kansas State College in  
partial fulfillment of the requirements for  
the Degree of Master of Science

by

**Edmond A. Morin, A. B.**

**Fort Hays Kansas State College**

Date

July 20, 1949

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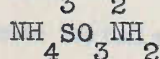
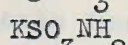
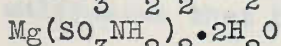
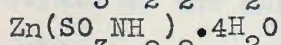
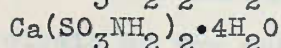
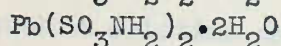
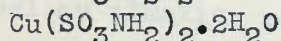
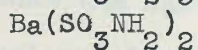
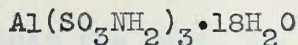
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## INTRODUCTION

Sulfamic acid at one time had no particular value, and very little was known about the physical and chemical properties of this acid. At the present time, however, this acid is a commercial product of considerable importance and extensive investigation has been conducted to discover its many chemical properties.

It is known that sulfamic acid reacts readily with basic oxides, hydroxides, and carbonates to yield the corresponding sulfamate salts (4). The amphoteric or acid metal oxides react less readily or not at all with the sulfamic acid. The acid is known to form highly soluble salts with basic hydroxides; for example, lead and barium sulfamates. Some sulfamates known to have been prepared are as follows:



Most of the metallic sulfamates show high solubility in water and most of them as indicated in the previous list are hydrated salts. The acid shows toxic effects such as might be expected of highly ionized acid material. Some of the sulfamates, such as ammonium sulfamate, are agreeable with cellulose and this has led to their extensive evolution of flameproofing agents (7).

A very interesting group of compounds derived from sulfamates are the aldehyde addition products (6). The aldehyde derivatives of calcium sulfamate were studied and had a particular interest because of their greater stability, especially in the isolated, solid form. The aldehyde addition products of calcium studied included benzaldehyde, furfuraldehyde, formaldehyde, acetaldehyde, and cinnamic aldehyde. These compounds have been described in patent literature, using essentially the method described by Schroeter.

It is known that the salts of sulfamic acid are more stable in neutral or alkaline solution than in the free acid and that such a solution may be evaporated by heating without hydrolysis of the amide group (1).

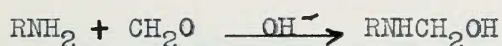
The metallic sulfamates that have been investigated as electroplating agents include nickel, cobalt, cadmium, zinc and copper. These metals have been satisfactorily plated in smooth deposits from sulfamic acid solution. (2).



With this information, the present investigation was carried out to determine methods of preparing aldehyde derivatives of those metals that had been investigated for electroplating, so that chemical composition, physical properties, and electroplating properties of these compounds might be studied.

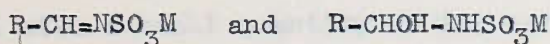
## GENERAL PRINCIPLES OF INVESTIGATION

The reactions of sulfamates with aldehydes are based on the assumption that both aliphatic and aromatic aldehyde react with aliphatic amines (13). Aliphatic amines can be methylated by heating with formaldehyde in the presence of acids, but if the reaction is carried out at room temperature and in the presence of alkali it takes another course. The reaction is an addition reaction and the methylol derivative can be isolated, thus:



The aldehydes which are known to react readily with amines are propionaldehyde, butyraldehyde, acetaldehyde, hydrocinnamic aldehyde, and phenylacetaldehyde. It is not known whether aldehyde ammonia is formed as an intermediate or whether it is condensed directly with the aldehyde through the enol form of the latter.

Some of the possible reactions of metallic sulfamates and aldehydes studied form methylene derivatives and some form methylol derivatives. Their structures are represented by the general formula respectively:



The letter "R" designates hydrogen or an organic group, and "M" represents a cation metal or group (8).

The reactions which have been investigated are calcium sulfamate and its aldehyde derivatives. Both hydroxyl (methylol) and dehydrated form (methylene) can be obtained, depending on the condition of preparation. The conditions of preparation were not given in the literature. The methylol derivative  $\text{Ca}(\text{HOCH}_2\text{NHSO}_3)_2$  has been isolated and showed high solubility in water. Also the methylene derivative  $\text{Ca}(\text{CH}_2\text{-NHSO}_3)_2$  has been isolated with indication of only moderate solubility in water (5).

#### Preparation of Metallic Sulfamates

Before the sulfamate salts were prepared, sulfamic acid was purified by dissolving approximately 125 g. of the crude acid in 300 ml. of water, previously heated to  $70^\circ \text{C}$ . (3). The solution was filtered three times with a subsequent lowering in temperature, each time the material crystallized out of its solution, all impurities were discarded. The final filtrate was cooled rapidly to the temperature of an ice salt mixture, and was then allowed to stand for twenty minutes. The crystals that formed were removed by suction filtration. The crystals were washed with a small quantity of ice water, then twice with cold ethanol and finally with ether. The product was air dried in an open dish for one hour and then

stored in a dark container.

The purified sulfamic acid was reacted in a concentrated solution with hydroxides of nickel, cadmium, cobalt, and carbonate of copper. The acid was added until the solution of bases became neutralized. Since the salts formed hydrates, they were not readily crystallized by addition of methanol or acetone. The salts were isolated by evaporation of the aqueous solution at room temperature. The metallic salts could have been evaporated under reduced pressure without breaking down the amide group.

#### Investigation of Properties and Composition

A number of analytical investigations were necessary to discover the type of substitution or addition in the reaction of metallic sulfamates with various aldehydes. These analyses were performed by determining the percentage composition of the metals, either by volumetric, gravimetric, or electrolytic method. The procedure used depended considerably on the activity of the metal being analyzed.

Sulfur determination was made by the use of the Parr Sulfur Bomb, Type 3 (flame ignition). After the fusion had taken place, the per cent of sulfur was found gravimetrically, by precipitation as barium sulfate.



Tests were made with potassium nitrite, this test to give evidence of some types of substitution in the amide group.

Most of the aldehyde derivatives contained water of crystallization. It was very important to classify these compounds according to the number of molecules of water which crystallize with one molecule of substance formed. The salt derivatives were found to be unstable to heat; thus, the water of crystallization was determined under reduced pressure and at a maximum temperature of 60° C.

The water of crystallization could not always be determined analytically by the above procedure but indirectly by a method based on the per cent of metal and sulfur found. If the analytical analysis correlated favorably the per cent found with the suspected percentage, then an assumption could be made from data obtained as to the number of molecules of water of crystallization present in the compounds formed.

The chief interest was to determine whether the aldehyde derivatives of metallic sulfamates (cobalt, nickel, cadmium, and copper) were good electroplating agents. The experiment was conducted with a simple electrolytic cell: plating cobalt salts on nickel, nickel salts on nickel, copper salts on copper, cadmium salts



on copper, and nickel salts on copper.

The methods by which the derivatives from the metallic sulfamates were reacted with aldehydes and their methods of analyses are described under the article heads respectively, "EXPERIMENTAL" and "ANALYTICAL AND CHEMICAL INVESTIGATION".

## EXPERIMENTAL

## Preparation and Properties of Aldehyde Derivatives

Cadmium Sulfamate

Cadmium sulfamate was reacted quantitatively with aldehydes by placing the salt in a flat-bottomed 250 ml. flask. The salt was dissolved in a small amount of distilled water and the reacted separately with a molecular or exact quantity of various aldehydes and the mixture was allowed to stand overnight. The aldehydes that did react showed an exothermic reaction. The aldehyde derivatives were isolated by evaporating at room temperature. Also the aldehyde derivatives could be isolated under reduced pressure without breaking down the amide group.

The aldehydes that reacted with cadmium sulfamate were formaldehyde, which produced a white crystalline hydrate; acetaldehyde gave a brownish sticky product which had no definite physical structure; propionaldehyde yielded a light brown crystalline product; furfuraldehyde reacted moderately to give an amorphous charcoal like compound.

The aldehydes that failed to react with the acid salt were benzaldehyde, isobutyraldehyde, and cinnamic aldehyde. For these aldehydes that failed to give

derivatives by the above mentioned procedure, modifications in the procedure were made. An attempt was made by warming the mixture on a steam bath 40-45° C. No reaction took place. The temperature was elevated to 60-70° C. but still no reaction was observed. A final attempt was made by trying to dissolve the cadmium sulfamate in alcohol and proceed with the aldehyde addition, but the salt failed to dissolve in alcohol.

#### Cobalt Sulfamate

Cobalt sulfamate was reacted quantitatively with a number of aldehydes. The salt was placed in a flat bottom 250 ml. flask. The salt was first dissolved in a minimum amount of water and then the aldehyde was added. The mixtures were allowed to stand overnight, and their derivatives were isolated by evaporating at room temperature; however, the derivatives might have been isolated under reduced pressure without breaking down the compound.

The aldehydes that formed derivatives were formaldehyde, acetaldehyde, furfuraldehyde and propionaldehyde. The formaldehyde gave a dark brown sticky product which had no definite crystalline shape; propionaldehyde gave a pink crystalline hydrate; furfuraldehyde reacted vigorously to give a charcoal like compound. All the derivatives were highly soluble in water except the

furfuraldehyde salt.

The aldehydes that failed to give results were benzaldehyde, isobutyraldehyde and cinnamic aldehyde.

### Copper Sulfamate

Copper sulfamate was mixed in quantitative proportions with formaldehyde, acetaldehyde, propionaldehyde, isobutyraldehyde, benzaldehyde, furfuraldehyde, and cinnamic aldehyde. The salt was placed in flat-bottomed 250 ml. flasks and dissolved in a minimum amount of water. This was followed by the addition of each of the aldehydes. The aldehydes that did react showed exothermic reaction. The mixtures were allowed to remain overnight and then their derivatives were isolated by evaporation at room temperature.

The aldehyde derivatives obtained were formaldehyde, acetaldehyde, furfuraldehyde, propionaldehyde. The formaldehyde salt formed a bluish crystalline hydrate; acetaldehyde yielded a dark greenish salt; propionaldehyde produced a somewhat greenish crystalline hydrate; furfural reacted to give a charcoal like product. The aldehyde derivatives were highly soluble in water with the exception of the furfuraldehyde salt. Their derivatives reacted slowly with potassium nitrite.

The aldehydes that failed to form any derivatives



were benzaldehyde, isobutyraldehyde and cinnamic aldehyde.

### Nickel Sulfamate

Quantitative reaction of nickel sulfamate was attempted with formaldehyde, acetaldehyde, propionaldehyde, isobutyraldehyde, furfuraldehyde, cinnamic aldehyde, and benzaldehyde. The salt was placed in flat-bottom 250 ml. flasks and dissolved in a minimum amount of water and the aldehyde added. The mixtures were allowed to set overnight; then the aldehyde salts were isolated at room temperature.

The aldehyde derivatives obtained were formaldehyde which gave a green crystalline hydrate; acetaldehyde which reacted to give a somewhat greenish like product; propionaldehyde gave a greenish crystalline hydrate; furfuraldehyde reacted to give a charcoal like compound. Their derivatives showed high solubility with water except furfuraldehyde salt, and the salts reacted very slowly with potassium nitrite.

The aldehydes that failed to give any derivatives were benzaldehyde, isobutyraldehyde and cinnamic aldehyde.

## ANALYTICAL AND CHEMICAL INVESTIGATION

### Determination of Per Cent of Water

Approximately 2 g. samples of each aldehyde



derivatives of cobalt, cadmium, nickel, and copper were placed in small crucibles and weighed analytically to four decimal places. The samples were placed under reduced pressure (one-third atmosphere) for forty-eight hours, and weighed. The loss in weight was not too noticeable, thus the water of crystallization could not be determined by direct weighing. Possibly if the experiment could have been conducted under 1 mm. pressure, satisfactory results might have been obtained without the decomposition of the amide group; but no satisfactory equipment was available to conduct this experiment under 1 mm. pressure.

The same sample of salts were placed in an oven for twenty-four hours, keeping the temperature at 40-60° C. The propionaldehyde salts seemed to lose their chemical structure at that temperature, and appears to have lost a little water. The acetaldehyde salts and formaldehyde salts did not lose enough water of crystallization to determine analytically the number of molecules of water which crystallized with one molecule of the aldehyde derivative. Their derivatives seemed to decompose at 60° C.

The number of molecules of water of crystallization could not be determined analytically by described procedures. The analyses were taken from the per cent of metal and sulfur found. With this percentage, an assumption could be

made as to the number of molecules of water in the aldehyde derivatives.

#### Determination of Cadmium

##### By Hydrogen Sulfide

Two-tenth gram samples of the aldehyde salts were dissolved in solutions containing enough sulfuric acid to make the solutions approximately six normal (19). The cadmium was precipitated out of the solution by passing hydrogen sulfide into the acid solution. The precipitate was filtered through a filtering crucible and washed several times with water; then the precipitate was dried at 110-120° C. The chemical factor used for cadmium was 0.77809. For some reason the results obtained ranged from six to seven per cent too high. The per cent of cadmium found by this means was discarded.

##### By Electrolysis

Two gram samples of the aldehyde derivatives were dissolved in an alkaline solution of NaOH containing enough hydroxyl ion to obtain a permanent red color by the use of phenolphthalein indicator (20). Then approximately 0.05N solution of potassium cyanide was added drop by drop until the cadmium hydroxide just dissolved. An excess of potassium cyanide was avoided. The solution

was ready for electrolysis. A platinum gauze electrode was used as the cathode and a spiral platinum wire was used as the anode. The electrolysis was conducted at 25° C. with a current of 0.5-0.8 ampere and voltage around 5 volts. During the electrolysis a magnetic stirrer was used to keep fresh material in contact with the electrodes, thus giving a firm adhering deposit. The current was maintained for thirty minutes and increased from 1 to 1.5 amperes; then the electrolysis was continued for two hours. The electrode was removed from the solution before the current was broken, and the cathode was immediately washed with water and ethyl alcohol. The cathode was dried at 100° C. for three minutes. The electrode was cooled and weighed.

Analysis of formaldehyde derivative of cadmium sulfamate:

Calculated for  $\text{Cd}(\text{SO}_3\text{NH}-\text{N}_2\text{COH})_2 \cdot 2\text{H}_2\text{O}$ ;  
Cd, 29.41%; Found Cd, 30.145%

Analysis of propionaldehyde derivative of cadmium sulfamate:

Calculated for  $\text{Cd}(\text{SO}_3\text{NCHCH}_2\text{CH}_3)_2 \cdot 2\text{H}_2\text{O}$ ;  
Cd, 26.66%; Found Cd, 25.88%.

#### By 8-Hydroxquinoline

A 1 g. sample of the aldehyde salt was dissolved in

a 500 ml. volumetric flask (16). With a 10 ml. pipette, portions were transferred to 250 ml. beakers. The solution was neutral, containing approximately 3 to 6 mg. of cadmium. Sodium carbonate solution was added until a slight turbidity was formed. Then acetic acid was added until the solution became clear. The solution was warmed and 3 to 5 g. of sodium acetate was added and then a slight excess of freshly prepared two per cent alcoholic solution of 8-hydroxyquinoline was added dropwise. The reagent was added until the yellow color of the supernatant solution appeared.

The solution was heated to 80-90° C. and then filtered through a filtering crucible. The precipitate was washed several times with warm and cold water. The precipitate was dried for several hours at 120-130° C. and weighed. The chemical factor used for the anhydrous compound  $\text{Cd}(\text{C}_9\text{H}_6\text{ON})_2$  was 0.2807. The per cent of cadmium was found from the equation:

$$\% \text{Cd} = \frac{\text{Wt. of Ppt.} \times \text{Chemical factor}}{\text{Wt. of Sample}} \times 100$$

Analysis of formaldehyde derivative of cadmium sulfamate:

Calculated for  $\text{Cd}(\text{SO}_3\text{NH}-\text{H}_2\text{COH})_2 \cdot \text{H}_2\text{O}$ ;  
Cd, 29.41%; Found Cd, 30.31%.



Analysis of propionaldehyde derivative of cadmium sulfamate:

Calculated for  $\text{Cd}(\text{SO}_3\text{N} = \text{CHCH}_2\text{CH}_3)_2 \cdot 2\text{H}_2\text{O}$ ;  
Cd, 26.66%; Found Cd, 26.15%.

#### Determination of Cobalt

By  $\alpha$ -Nitroso- $\beta$ -Naphthol

Reagent: Two grams of the solid  $\alpha$ -nitroso- $\beta$ -naphthol was dissolved in 100 ml. of glacial acetic acid and diluted with 100 ml. of hot water and filtered (18).

Five-tenth grams of the sample was dissolved in a 500 ml. volumetric flask. Then with a clean, dry 50 ml. pipet, aliquot portions were transferred into each of two 400 ml. beakers containing very little hydrochloric acid (three drops). Approximately 10-12 drops of 30% hydrogen peroxide (Perhydrol) were added and a sufficient amount of sodium hydroxide was added to precipitate all the cobalt as  $\text{Co}(\text{OH})_3$ . Precautions were taken not to add an excess of sodium hydroxide. The precipitate was dissolved by adding approximately 10 ml. of glacial acetic acid, and diluted with hot water to 150-200 ml.  $\alpha$ -Nitroso- $\beta$ -naphthol was added in excess (50%). The mixture was stirred and heated to boiling. The precipitate was allowed to settle and then was filtered through a filtering crucible. The precipitate was washed three times with 30% acetic acid solution and finally with water. It was dried



at 130-135° C. and weighed. The chemical factor used for cobalt was 0.09463. The per cent of cobalt was found by this equation:

$$\%Co = \frac{\text{Chemical factor} \times \text{Wt. of Ppt.} \times 100}{\text{Wt. of Sample}}$$

Analysis of formaldehyde derivative of cobalt sulfamate:

Calculated for  $Co(SO_3NH-H_2COH)_2 \cdot H_2O$ ;

Co, 16.88%; Found Co, 17.27%. Calculated for anhydrous salt: Co, 17.73%.

#### By Electrolysis

A one gram sample of the aldehyde salt was dissolved in an ammoniacal solution containing ammonium sulfate. The type of electrode used was a hollow cylinder platinum gauze cathode, and the anode, a platinum spiral wire (15). The solution was stirred by a magnetic stirrer. The electrolysis was conducted at a current of 0.5 amp. for thirty minutes and increased from 1 to 2 amp. for a period of three hours. The deposition was not complete and no quantitative results were obtained from this type of procedure.

## Determination of Copper

By Iodimetry Titration

A standard solution of thiosulfate was prepared against a known standard of iodine solution. The concentration was approximately 0.05 normal (10).

A two-tenths gram sample of the aldehyde salt was dissolved in a 3-4 pH buffer solution (12). This buffer solution was prepared by dissolving 21.6 g. of citric acid in one liter of distilled water and dissolving 71.6 g. of sodium bisulfate (containing twelve molecules of water) in one liter of distilled water; then 615 ml. of citric acid was added to 385 ml. of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  to make the required pH. Twenty-five milliliter of potassium iodide solution containing 4-5 g. of salt was added to the buffer solution containing the known weight of sample. The mixture was allowed to stand for several minutes before titration. The liberated iodine was titrated with the known normality of thiosulfate solution. When the color of liberated iodine almost faded away, one to two grams of potassium thiocyanate were added just prior to the addition of starch solution. Just as the iodine faded away 5 ml. of starch solution was added and the titration was completed when one drop of thiosulfate solution caused disappearance of the blue color. The

end point was difficult to recognize and some time was required to find the end point of the titration. The per cent of copper was found by using the equation:

$$\%Cu = \frac{\text{ml.} \times N \times \text{Milliequivalent of Cu} \times 100}{\text{Wt. of Sample}}$$

Analysis of formaldehyde derivative of copper sulfamate:

Calculated for  $\text{Cu}(\text{SO}_3\text{NH}-\text{H}_2\text{COH})_2 \cdot 5\text{H}_2\text{O}$ ;

Cu, 15.62%; Found Cu, 15.49%.

Analysis of acetaldehyde derivative of copper sulfamate:

Calculated for  $\text{Cu}(\text{SO}_3\text{N}=\text{CHCH}_3)_2 \cdot 3\text{H}_2\text{O}$ ;

Cu, 17.34%; Found Cu, 17.05%.

Analysis of propionaldehyde derivative of copper sulfamate:

Calculated for  $\text{Cu}(\text{SO}_3\text{N}=\text{CHCH}_2\text{CH}_3)_2$ ;

Cu, 18.90%; Found Cu, 19.86%.

#### By Electrolysis

Two gram samples of the aldehyde salts were dissolved in electrolytic beakers containing approximately 150 ml. of water with 12 ml. of phosphoric acid (85) (14). The type of electrode used was a hollow cylinder platinum gauze cathode, and the anode a platinum spiral wire. The solution was stirred with a magnetic stirrer to keep fresh material in contact with the electrodes, thus giving a firm

adhering deposit. The electrolysis was conducted at a current of two amperes for two hours. After the electrolysis was completed the cathode was carefully removed from the solution without breaking the current. The cathode was dipped into a beaker of clean distilled water and finally washed with ethyl alcohol. The cathode was dried at 105° C. for three minutes. The electrode was cooled and weighed.

$$\%Cu = \frac{\text{Wt. of deposit}}{\text{Wt. of sample}} \times 100$$

Analysis of formaldehyde derivative of copper sulfamate:

Calculated for  $Cu(SO_3NH-CH_2OH) \cdot 5H_2O$ ;

Cu, 15.62%; Found Cu, 15.49%.

Analysis of acetaldehyde derivative of copper sulfamate:

Calculated for  $Cu(SO_3N=CHCH_3)_2 \cdot 3H_2O$ ;

Cu, 17.34%; Found Cu, 17.05%.

Analysis of propionaldehyde derivative of copper sulfamate:

Calculated for  $Cu(SO_3N=CHCH_2CH_3)_2$ ;

Cu, 18.09%; Found Cu, 19.86%.



## Determination of Nickel

### By Dimethylglyoxime

One gram of dimethylglyoxime was dissolved in 99 g. of alcohol solution to prepare the reagent.

A one-tenth gram sample of the aldehyde salt was dissolved in 50 ml. of distilled water (neutral). When dimethylglyoxime was added to the neutral solution, it precipitated as a red flocculent precipitate (17). Precautions were taken so that the nickel ion did not exceed over 30-35 mg. because of the bulkiness of the nickel dimethylglyoxime precipitate. Also care was taken during the process of precipitation so that not more than five per cent excess of the alcohol solution of dimethylglyoxime was added; otherwise contamination might have resulted due to the insolubility of dimethylglyoxime in water. The precipitate was filtered through a filtering crucible. The precipitate was washed with one milliliter of alcohol. The precipitate of nickel dimethylglyoxime was dried at 110-120° C. and weighed as such. The chemical factor used for nickel was 0.2032. The per cent of nickel was found by the use of the equation:

$$\%Ni = \frac{\text{Chemical factor} \times \text{Wt. of Precipitate} \times 100}{\text{Wt. of Sample}}$$



Analysis of formaldehyde derivative of nickel sulfamate:

Calculated for  $\text{Ni}(\text{SO}_3\text{NH}-\text{CH}_2\text{OH})_2 \cdot 6\text{H}_2\text{O}$ ;

Ni, 13.73%; Found Ni, 14.58%

Calculation for  $5\text{H}_2\text{O}$ :

Ni, 14.61%.

Analysis of acetaldehyde derivative of nickel sulfamate:

Calculated for  $\text{Ni}(\text{SO}_3\text{N}=\text{CHCH}_3)_2 \cdot 4\text{H}_2\text{O}$ ;

Ni, 15.65%; Found Ni, 15.55%.

Analysis of propionaldehyde derivative of nickel sulfamate:

Calculated for  $\text{Ni}(\text{SO}_3\text{N}=\text{CHCH}_2\text{CH}_3)_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ ;

Ni, 16.39%; Found Ni, 16.63%.

#### By Electrolysis

A one gram sample of the aldehyde salt was dissolved in an ammoniacal solution containing 4-5 g. of ammonium sulfate (21). The Type of electrode used was the round cylinder platinum gauze cathode and the anode a platinum spiral wire. The electrolysis was conducted at a current of 1 to 2 amp. for three hours. A magnetic stirrer was used to stir the solution so as to keep fresh material in contact with the electrodes, thus giving a firm adhering deposit. After the electrolysis was completed the cathode was removed carefully from the solution without breaking the current.

The cathode was washed with clean distilled water and with ethyl alcohol. The cathode was dried at 100° C. for three minutes. The electrode was cooled and weighed as such.

$$\%Ni = \frac{\text{Wt. of deposit}}{\text{Wt. of Sample}} \times 100$$

Analysis of formaldehyde derivative of nickel sulfamate:

Calculated for Ni  $(SO_3NH-CH_2OH)_2 \cdot 6H_2O$ ;

Ni, 13.73%; Found Ni, 15.42%.

Calculation for  $5H_2O$ :

Ni, 14.61%.

#### Determination of Sulfur

##### By Barium Sulfate

The Parr Sulfur Bomb, Type 3 (flame ignition) was used for the determination of per cent of sulfur for various aldehyde salts (11).

Approximately one gram of potassium perchlorate (accelerator) and a five-tenth gram sample of the aldehyde salt: previously dried at 60° C. for three hours, was placed in the fusion cup. The mixture was mixed thoroughly, so as to leave no lumps of potassium perchlorate. One measure of sodium peroxide was then added quickly (approximately 15 g.) to the fusion cup and mixed

thoroughly. The bomb was assembled and the screw cap tightened firmly. The charge was ignited by placing the bomb in the ignition housing over a sharp flame. Water was placed in the bomb cover recess. After the water had boiled on the bomb cover recess, the flame was removed immediately. The bomb was allowed to cool for three minutes before quenching. After the bomb had cooled down, it was dismantled and the fusion was dissolved in 100 ml. of hot distilled water. The cover and fusion cup were washed with a hot stream of distilled water. The fusion solution contained metal oxide precipitate and this was filtered with fast filter paper. The filtrate was used to determine the per cent of sulfur by precipitating as barium sulfate.

Concentrated hydrochloric acid was added to the filtrate until the neutral point was reached with phenolphthalein. After bringing to the neutral point, 1 to 2 ml. of the acid was added in excess. Then 25 ml. of a saturated solution of picric acid were added. The effect of such addition seemed to produce crystals of barium sulfate which settled more rapidly and it was also noticed that the precipitate was much more easy to filter and wash.

The acid solution was heated nearly to boiling and then approximately 20 ml. in excess of the calculated

amount of hot 0.2 N barium chloride was added (9). The beaker was set on a hot place (70-80° C.) until the precipitate became crystalline in structure (5-6 hours). The barium sulfate was filtered through a filtering crucible. The precipitate was washed with hot distilled water until no positive test for chloride was given with silver nitrate solution. The precipitate was dried at 600-650° C. for three hours and weighed as such.

The per cent of sulfur was calculated by the use of this equation:

$$\% \text{Sulfur} = \frac{0.1374 \times \text{Wt. of BaSO}_4}{\text{Wt. of Sample}} \times 100$$

Analysis of formaldehyde derivative of cobalt sulfamate:

Calculated for  $\text{Co}(\text{SO}_3\text{NH-CH}_2\text{OH})_2$ ;  
S, 20.61%; Found S, 19.14%.

Analysis of formaldehyde derivative of copper sulfamate:

Calculated for  $\text{Cu}(\text{SO}_3\text{NH-CH}_2\text{OH})_2$ ;  
S, 20.30%; Found S, 19.75%.

Analysis of propionaldehyde derivative of nickel sulfamate:

Calculated for  $\text{Ni}(\text{SO}_3\text{N=CHCH}_2\text{CH}_3)_2$ ;  
S, 19.68%; Found S, 19.19%.



Analysis of acetaldehyde derivative of copper sulfamate:

Calculated for  $\text{Cu}(\text{SO}_3\text{N}=\text{CHCH}_3)_2$ ;

S, 20.25%; Found S, 19.41%.

FIGURE 1. PLATINGS FROM CADMIUM SALTS.



Formol derivative of  
cadmium sulfamate  
Plate on copper  
25-30° C  
0.5 amp/cm<sup>2</sup>  
Dense, tenacious.



Formol derivative of  
cadmium sulfamate  
Plate on copper  
40-45° C  
0.5 amp/cm<sup>2</sup>  
Dense, loose.



Formol derivative of  
cadmium sulfamate  
Plate on copper  
25-30° C  
1.0 amp/cm<sup>2</sup>  
Dense, loose.



Formol derivative of  
cadmium sulfamate  
Plate on copper  
60-65° C  
1.5 amp/cm<sup>2</sup>  
Dense, loose.



Propional derivative  
of cadmium sulfamate  
Plate on copper  
25-30° C  
0.2 amp/cm<sup>2</sup>  
Dense, tenacious.



Propional derivative  
of cadmium sulfamate  
Plate on copper  
60-65° C  
0.2 amp/cm<sup>2</sup>  
Powdery, loose.



Propional derivative  
of cadmium sulfamate  
Plate on copper  
25-30° C  
1.25 amp/cm<sup>2</sup>  
Dense, loose.

FIGURE 2. PLATINGS FROM COBALT SALTS



Formol derivative of  
cobalt sulfamate  
Plate on nickel  
25-30° C  
0.5 amp/cm<sup>2</sup>  
Dense, loose. . .



Formol derivative of  
cobalt sulfamate  
Plate on nickel  
25-30° C  
0.3 amp/cm<sup>2</sup>  
Dense, tenacious.



Formol derivative of  
cobalt sulfamate  
Plate on nickel  
25-30° C  
1.5 amp/cm<sup>2</sup>  
Dense, loose.



Propional derivative  
of cobalt sulfamate  
Plate on nickel  
30-35° C  
0.2 amp/cm<sup>2</sup>  
Dense, loose.



Propional derivative  
of cobalt sulfamate  
Plate on nickel  
35-40° C  
1.7 amp/cm<sup>2</sup>  
Dense, loose.



Propional derivative  
of cobalt sulfamate  
Plate on nickel  
50-65° C  
2.75 amp/cm<sup>2</sup>  
Dense, loose.

FIGURE 3. PLATINGS FROM COPPER SALTS



Formol derivative of  
copper sulfamate  
Plate on copper  
25-30° C  
0.25 amp/cm<sup>2</sup>  
Dense, tenacious.



Formol derivative of  
copper sulfamate  
Plate on copper  
25-30° C  
0.5 amp/cm<sup>2</sup>  
Dense, loose.



Formol derivative of  
copper sulfamate  
Plate on copper  
30-35° C  
0.4 amp/cm<sup>2</sup>  
Dense, loose.



Formol derivative of  
copper sulfamate  
Plate on copper  
40-45° C  
0.6 amp/cm<sup>2</sup>  
Powdery, loose.



Propional derivative  
of copper sulfamate  
Plate on copper  
25-30° C  
0.075 amp/cm<sup>2</sup>  
Dense, tenacious.



Propional derivative  
of copper sulfamate  
Plate on copper  
30-35° C  
0.1 amp/cm<sup>2</sup>  
Dense, tenacious.



Propional derivative  
of copper sulfamate  
Plate on copper  
50-55° C  
1.5 amp/cm<sup>2</sup>  
Powdery, loose.



FIGURE 4. PLATINGS FROM NICKEL SALTS



Formol derivative of  
nickel sulfamate  
Plate on copper  
25-30° C  
0.1 amp/cm<sup>2</sup>  
Dense, tenacious.



Formol derivative of  
nickel sulfamate  
Plate on copper  
25-30° C  
0.2 amp/cm<sup>2</sup>  
Dense, tenacious.



Formol derivative of  
nickel sulfamate  
Plate on copper  
25-30° C  
0.5 amp/cm<sup>2</sup>  
Dense, tenacious.



Formol derivative of  
nickel sulfamate  
Plate on copper  
25-30° C  
1.25 amp/cm<sup>2</sup>  
Dense, tenacious



Propional derivative  
of nickel sulfamate  
Plate on copper  
25-30° C  
0.4 amp/cm<sup>2</sup>  
Dense, tenacious.



Propional derivative  
of nickel sulfamate  
Plate on copper  
35-40° C  
1.0 amp/cm<sup>2</sup>  
Dense, tenacious.



Propional derivative  
of nickel sulfamate  
Plate on copper  
45-60° C  
1.5 amp/cm<sup>2</sup>  
Dense, tenacious.

FIGURE 5. PLATINGS FROM NICKEL SALTS



Formol derivative of  
nickel sulfamate  
Plate on nickel  
25-30° C  
0.2 amp/cm<sup>2</sup>  
Dense, loose.



Formol derivative of  
nickel sulfamate  
Plate on nickel  
25-30° C  
0.5 amp/cm<sup>2</sup>  
Dense, tenacious.



Formol derivative of  
nickel sulfamate  
Plate on nickel  
45-50° C  
1.5 amp/cm<sup>2</sup>  
Dense, tenacious.



Formol derivative of  
nickel sulfamate  
Plate on nickel  
50-60° C  
1.0 amp/cm<sup>2</sup>  
Dense, tenacious.



Propional derivative  
of nickel sulfamate  
Plate on nickel  
25-30° C  
0.33 amp/cm<sup>2</sup>  
Dense, loose.



Propional derivative  
of nickel sulfamate  
Plate on nickel  
25-30° C  
0.5 amp/cm<sup>2</sup>  
Dense, loose.



Propional derivative  
of nickel sulfamate  
Plate on nickel  
30-40° C  
0.66 amp/cm<sup>2</sup>  
Dense, loose.

## PROPERTIES OF THE ELECTROPLATINGS

Test platings were made of the various derivatives to discover whether they might be used to give deposits satisfactory for commercial electroplating. Photographs of the platings were made and are included on pages 28 to 32.

The writer has employed the name propionaldehyde derivatives of metallic sulfamates throughout the research. Notice that on the figures, however, the official name propional derivative is used. This practice was chosen to conserve space and exhibit uniformity. Thus the reader should not confuse this with misuse of the word propional derivative.

The electroplatings were performed with a 400-ml electrolytic beaker at various current densities and temperatures. The concentration of the salt bath employed was approximately 0.01 Molar solution.

In figure (1), cadmium was plated on copper. It seems that low temperatures (25-30° C) and low current densities give a fairly tenacious deposit, while high temperatures and current densities give loose and powdery deposits. Potassium cyanide was used as the electrolyte.

In figure (2), cobalt was plated on nickel. Cobalt was deposited from an ammoniacal solution of ammonium sulfate. At very high current densities and high

temperatures unsatisfactory deposits were obtained (loose deposit); however, a very low current density (0.3 amp/cm<sup>2</sup>) gave a fairly tenacious deposit.

In figure (3), copper was plated on copper. Copper was deposited from a phosphoric acid (85%) solution at high and low current densities at various temperatures. Fair deposits were attained at low temperatures (25-30° C) and low current densities, while high temperatures (above 30° C) and high current densities (above 0.2 amp/cm<sup>2</sup>) gave loose and powdery deposits.

In figure (4), nickel was plated on copper. Nickel was deposited from a phosphoric acid (85%) solution. Good tenacious deposits were obtained at low current densities and low temperatures (25-30° C), while fair deposits were obtained at high current densities (above 0.5 amp/cm<sup>2</sup>) and high temperatures (above 30° C).

In figure (5), nickel was plated on nickel. Nickel was deposited from a phosphoric acid (85%) solution. This was the most peculiar deposit. The writer will not attempt to explain the unusual deposit of nickel on nickel. It appears that high temperatures (above 40° C) and high current densities gave fairly tenacious deposits, while low temperatures (25-35° C) and low current densities gave loose deposits.



## CONCLUSIONS IN REGARD TO STRUCTURE

The chemical structure of the aldehyde derivatives of metallic sulfamates (cobalt, nickel, cadmium, and copper) exhibited different types of addition products. From the data obtained, it appears that the formaldehyde salts have an hydroxyl or methylol derivative. The formaldehyde salt derivatives can be represented by this general formula,  $M(\text{SO}_3\text{NH}-\text{CH}_2\text{OH})_2$ . Acetaldehyde and propionaldehyde derivatives appear to have the dehydrated or methylene form; thus, the general formula can be represented as,  $M(\text{SO}_3\text{N}=\text{CHCH}_3)_2$  and  $M(\text{SO}_3\text{N}=\text{CHCH}_2\text{CH}_3)_2$ . The letter "M" designates either cobalt, nickel, cadmium, or copper.

Analyses could not be made of the furfuraldehyde derivatives, due to its insolubility in water and mineral acids.

## SUMMARY

From the metallic sulfamates studied, it appears that the straight chain aliphatic aldehydes react moderately, including formaldehyde, acetaldehyde, and propionaldehyde; while aromatic aldehydes and long chain aliphatic aldehydes (beyond propionaldehyde) appear not to react with the metallic salts under conditions studied. Furfuraldehyde reacts moderately to give a derivative. The nature of its chemical structure from analysis could not be made, due to the insolubility of the salt in water and mineral acids.

The formaldehyde derivatives gave typical characteristics of the cobalt, nickel, copper and cadmium salts while the higher derivatives did not exhibit this relationship.

The acetaldehyde derivatives had a small amount of impurities. The salts could not be purified with the acetone, methanol, acetone-methanol mixture, or ether. The analytical analysis of cobalt and cadmium derivatives of acetaldehyde gave considerably variable results and the data was discarded.

The acetaldehyde and propionaldehyde derivatives have a tendency to lose a molecule of water from each amide linkage, consequently introducing the methylene derivative. It is rather difficult to remove water of

crystallization from the derivatives (acetaldehyde and propionaldehyde) without decomposing the compound.

As a whole, the deposition by electrolysis of the metallic sulfamates of aldehyde derivatives were not too good as electroplating agents under the experimental conditions investigated, although, the platings of the nickel salts on copper gave smooth adhering deposit at low and high current densities.

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