

is obviated. In order to avoid sparking, the regulator should be used with a current of very low amperage (0.01 amp. or less) which actuates a relay. The heating current can not be passed through the apparatus.

To adjust the regulator, a small quantity of mercury is shaken from the auxiliary bulb into the stem or from the stem into the bulb, according to whether adjustment for a lower or higher temperature is desired. The capillary connection *h* should be rather narrow, as otherwise it is not possible to transfer sufficiently small globules of mercury to effect an accurate adjustment. The adjustment is greatly facilitated by the graduation on the stem. When the regulator is brought to the desired temperature by means of a water bath, the number of graduations between the level of the mercury column and the wire *d* will indicate the quantity of mercury which must be transferred from the stem to the auxiliary bulb, or conversely. The transfer may be made after the regulator has returned to room temperature. The form of the main "bulb" of the regulator is, of course, immaterial and may be varied according to requirements. In the type illustrated, the bulb consists of a large tube 1 cm. in diameter with three small tubes each 10 cm. long. This form has been found very convenient where the regulator is placed directly in the chamber to be controlled. Where the temperature is indirectly controlled, as in the water jacketed incubators in common use in laboratories, an oblong bulb would be more convenient. In the regulator illustrated, the volume of the mercury up to point of contact *d* is about 20 cc. The increase in volume per degree would be 0.0036 cc. The diameter of the capillary *f* is about 0.16 cm. Its cross-section would, therefore, be 0.02 sq. cm. The linear expansion in the capillary per degree centigrade would be 0.18 cm. The length of the capillary is 5 cm., its volume 0.1 cc. This volume of mercury would correspond to the expansion of 20 cc. of mercury caused by a rise through 28°. The volume of the bulb *g* is about 0.5 cc., allowing a possible temperature range of over 100°.

The apparatus was constructed for the writers by E. Machlett & Son, 153 East 84th St., New York, N. Y.

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## ON THE STEARATES AND PALMITATES OF THE HEAVY METALS WITH REMARKS CONCERNING INSTANTANEOUS PRECIPITATIONS IN INSULATING SOLUTIONS.

BY ALFRED E. KOENIG.  
Received February 26, 1914.

### Introduction.

The stearates and palmitates of the heavy metals have been known for a long time. Brief accounts of their preparation and analysis are found

in Chevreul's "Les Corps Gras" and in Liebig's *Annalen*.<sup>1</sup> But little further work has been done on them.

Kahlenberg<sup>2</sup> has performed many experiments to show that all types of chemical reactions which take place in conducting solutions, and are attributed to the ionization of the compounds entering into the reaction, may be duplicated in non-conducting solutions. For these experiments it was necessary to employ organic solvents, and in most of these the stearates, palmitates, and oleates of the heavy metals dissolve. This is due to their high carbon content, as Kahlenberg has pointed out. The oleates have been most frequently used, but, since they are generally of a smeary consistency, they present many experimental difficulties. The stearates and palmitates of the heavy metals, because of their higher melting points, can readily be reduced to a powder and thoroughly dried. They therefore lend themselves much more satisfactorily to various purposes.

The work described in this paper was undertaken to investigate further the properties of the stearates and palmitates of the heavy metals and also the solutions of these salts.

### Experimental.

*Preparation of the Salts and Instantaneous Precipitations in Their Solutions.*—Merck's palmitic and stearic acids were used in the preparation of the stearates and palmitates. The chlorides and sulfates of the heavy metals were also from the same source. The pyridine, benzene, toluene, carbon tetrachloride, and other solvents employed in this work, were of Merck's best grade.

The copper, cadmium, cobalt, chromium, iron, lead, manganese, mercury, nickel and zinc salts were prepared according to the following general method: About 15 g. of the sodium soap were dissolved in a liter of warm water. This always yielded a clear solution, whereas, if the soap was placed in cold water and then warmed, a cloudy liquid would be obtained. The clear liquid, prepared as just described, sets to a solid jelly if allowed to cool. The warm solution of the soap was poured into an excess of a 1% solution of the chloride or sulfate of the heavy metal, with vigorous stirring. The flocculent precipitate of the heavy metal soap was washed by decantation until the washings were found to be free from soluble salts. The stearates and palmitates were dried in an air bath at 115° to 120° for ten to twelve hours. The flat crystallizing dishes in which the salts were dried were so large that the resulting clear liquid, which in cooling solidified to a glassy solid, formed a layer not more than a millimeter thick. The salts were powdered and kept in glass stoppered bottles till used.

<sup>1</sup> *Ann.*, 35, 51 (1840); 36, 44 (1840); 84, 297 (1851), and 88, 298 (1853).

<sup>2</sup> *J. Phys. Chem.*, 6, 1 (1902).

For the preparation of the sodium soaps, a quantity of the fatty acid was added to a *little less than* its equivalent of  $N/2$  NaOH solution in a flask provided with a reflux condenser, and was then heated on a steam bath for ten to twelve hours. The clear solution was filtered through cotton, which retained the small globules of uncombined acid. This procedure is quite essential to avoid the formation of basic salts, when the heavy metal salts are precipitated by means of the sodium soaps. Cady<sup>1</sup> in a recent article, states that when a dehydrated solution of copper oleate in benzene and one of hydrochloric acid in benzene, both of which have an extremely low conductivity, are mixed there results an instantaneous precipitation of copper chloride, accompanied by a large increase in the conductivity of the resulting solution. This latter phenomenon is contrary to that observed by Kahlenberg.<sup>2</sup> The increased conductivity, observed by Cady, may be due to the different manner of preparing the copper oleate. In Cady's method, oleic acid was neutralized with an *excess* of sodium hydroxide. When this sodium oleate solution is used for the precipitation of copper oleate, a basic copper oleate is necessarily formed. The reaction of the basic oleate with hydrochloric acid would result in the formation of a certain amount of water which with the hydrochloric acid present would cause an increase in the conductivity of the solution.

Kahlenberg<sup>2</sup> has pointed out that many reactions of the type of double decompositions take place as readily in non-aqueous solvents as in water. I found that such a reaction occurred when a solution of cupric stearate in benzene was brought together with a solution of stannic chloride in the same solvent. An *instantaneous* precipitate of cupric chloride was formed. The clear filtrate was heated on a water bath to distil off the excess of stannic chloride and the benzene. A light yellow liquid remained in the retort which solidified at about 50°. On analysis this yielded 15.06% of stannic oxide and the results of three analyses, one of which was of a sample prepared at a different time, checked very closely. This would indicate a basic stannic stearate, of the formula  $\text{Sn}(\text{C}_{17}\text{H}_{35}\text{COO})_4 \cdot \text{SnO} \cdot (\text{C}_{17}\text{H}_{35}\text{COO})_2$ . Likewise a benzene solution of silicon tetrachloride run into a benzene solution of cupric palmitate formed an instantaneous precipitate of cupric chloride. The colorless filtrate on evaporation at room temperature left a gelatin-like solid which charred only slightly on ignition, and yielded 82.3% of  $\text{SiO}_2$ . This would show that if a silicon palmitate was formed at all, it was a basic salt as might be expected, but the matter was not investigated any further.

The fact that instantaneous precipitation of cupric chloride thus occurs in benzene solutions of cupric stearate and cupric palmitate shows conclu-

<sup>1</sup> THIS JOURNAL, 35, 1434 (1913).

<sup>2</sup> J. Phys. Chem., 6, 1 (1902).

sively that such phenomena are not due to the unsaturated condition of the acid radical, for the stearic and palmitic acids are saturated compounds. This then conclusively refutes Cady's<sup>1</sup> claim that the unsaturated condition of the oleates is the cause for similar instantaneous precipitations in their solutions.

*Solubilities.*—To determine the qualitative solubility of the salts that were prepared, a portion of the finely powdered salt was placed in a test tube and shaken with a few cubic centimeters of the solvent. After standing for several hours, a portion of the liquid was evaporated on a watch glass. The solubility in the hot solvent was determined in the same way after the lightly corked test tube containing the salt and the liquid had been warmed on a steam bath for an hour. The results have been placed in Table I. In this table (S) indicates that the salt is soluble to the extent

TABLE I.

Solvent.	Chromium stearate.	Copper stearate.	Copper palmitate.	Cobalt stearate.	Cobalt palmitate.	Nickel stearate.	Manganese stearate.	Stannic stearate.
Pyridine, cold.....	S	S	S	S	S	S	S	S
Pyridine, hot.....	S	S	S	S	S	S	S	S
Benzene, cold.....	I	I	I	s	s	S	I	s
Benzene, hot.....	s	S	S	S	S	S	s	S
Toluene, cold.....	I	I	I	s	s	S	s	S
Toluene, hot.....	s	S	S	S	S	S	S	S
Carbon bisulfide, cold.....	s	I	I	s	s	S	s	S
Carbon bisulfide, hot.....	S	S	S	s	s	S	s	S
Chloroform, cold.....	s	s	s	S	S	S	I	S
Chloroform, hot.....	S	S	S	S	S	S	I	S
Carbon tetrachloride, cold.....	s	s	s	S	S	S	I	S
Carbon tetrachloride, hot.....	S	S	S	S	S	S	I	S
Amyl alcohol, cold.....	I	S	S	S	S	S	I	S
Amyl alcohol, hot.....	I	S	S	S	S	S	I	S
Methyl alcohol, cold.....	I	I	I	I	I	I	I	S
Methyl alcohol, hot.....	I	I	I	I	I	s	I	S
Ether, cold.....	I	I	I	s	s	I	I	—
Ether, hot.....	I	I	I	s	s	S	I	—
Acetone, cold.....	s	I	I	I	I	I	I	S
Acetone, hot.....	s	I	I	I	I	s	I	S
Ethyl acetate, cold.....	s	s	s	I	I	I	I	—
Ethyl acetate, hot.....	s	S	S	I	I	I	I	—
Paraffin, cold.....	S	S	S	S	S	S	S	S
Paraffin, hot.....	S	S	S	S	S	S	S	S
Heptane, cold.....	I	s	s	s	s	s	I	I
Heptane, hot.....	I	S	S	S	S	S	I	s

<sup>1</sup> *Loc. cit.*

of about 1% or more; (s) indicates that only a few hundredths of a % dissolved, and (I) that the salt is insoluble.

As Table I shows, the cobalt, copper, and nickel stearates and palmitates were insoluble, or only slightly soluble, in cold benzene, toluene, heptane, chloroform, and carbon tetrachloride. When warmed for some time with these liquids, 1-2% solutions may be obtained. From solutions in these solvents, the salts did not separate on cooling. The whole liquid always set to a homogeneous jelly. Thus a 1% solution of stannic stearate in methyl alcohol yielded a jelly, showing that this salt behaves like the stearates of the other heavy metals. Kahlenberg<sup>1</sup> has shown that copper oleate is soluble in cold benzene. Since the copper salts of stearic and palmitic acids were found to be insoluble in this solvent, these facts might be used to separate these acids from oleic acid.

All the stearates and palmitates were found to be copiously soluble in hot pyridine. Some of these hot saturated solutions on cooling deposited distinctly crystalline addition products of the heavy metal soaps with pyridine. A hot saturated solution of copper stearate, or palmitate, was of a deep bluish green color which turned to a deep blue on cooling and yielded a crop of green rectangular plates or granular masses. The mother liquor on standing deposited deep blue, feathery crystals in radiating clusters. A solution partly saturated at 80°, and allowed to cool very slowly, solidified almost entirely to a mass of light blue needles. The green crystals were quite stable and did not effloresce on exposure to the air for several weeks. They were found to contain one molecule of the copper soap combined with one of pyridine  $(\text{Cu}(\text{C}_{17}\text{H}_{35}\text{COO})_2 \cdot \text{C}_5\text{H}_5\text{N}$  and  $\text{Cu}(\text{C}_{15}\text{H}_{31}\text{COO})_2 \cdot \text{C}_5\text{H}_5\text{N}$ . The deep blue crystals were fairly stable but changed to an amorphous powder on exposure to the air. They were found to contain two molecules of pyridine to one of the soap. The light blue needles, when placed on a porous plate, quickly lost their pyridine and with it their crystalline form. Their composition has not been ascertained.

A hot, saturated solution of the stearate or palmitate, of cobalt was a deep red color. This on cooling yielded rose colored plates which were found to contain two molecules of the pyridine to one of the cobalt salt. The crystals effloresced slowly to a pink amorphous powder.

The hot, saturated solution of the nickel stearate has a light green color similar to that of an aqueous solution of nickel chloride. This solution yielded green crystalline plates that appeared a bluish green when the excess of mother liquor had drained off. These crystals were stable, and were found to contain two molecules of pyridine to one of the stearate.

All of these crystalline products have a well defined melting point, whereas the soaps themselves do not, as is shown by the following table:

<sup>1</sup> *J. Phys. Chem.*, 6, 1 (1902).

TABLE II.—THE MELTING POINTS OF THE PURE SOAPS AND OF THEIR CRYSTALLINE COMPOUNDS WITH PYRIDINE.

Soaps.	M. p.	Crystalline products.	M. p.
Copper stearate.....	115-125°	$\text{Cu}(\text{C}_{17}\text{H}_{35}\text{COO})_2 \cdot \text{C}_5\text{H}_5\text{N}$	87.0°
Copper palmitate.....	115-120°	$\text{Cu}(\text{C}_{15}\text{H}_{31}\text{COO})_2 \cdot \text{C}_5\text{H}_5\text{N}$	86.6°
Cobalt stearate.....	73- 75°	$\text{Co}(\text{C}_{17}\text{H}_{35}\text{COO})_2 \cdot 2\text{C}_5\text{H}_5\text{N}$	70.4°
Cobalt palmitate.....	70- 75°	$\text{Co}(\text{C}_{15}\text{H}_{31}\text{COO})_2 \cdot 2\text{C}_5\text{H}_5\text{N}$	64.0°
Nickel stearate.....	80- 86°	$\text{Ni}(\text{C}_{17}\text{H}_{35}\text{COO})_2 \cdot 2\text{C}_5\text{H}_5\text{N}$	85.4°

After having obtained several crops of crystals from the solution of the copper soap, the remaining liquid no longer had the same color as a fresh solution but became a dark green. It then deposited a light blue crystalline crust, together with a brownish slimy precipitate. The solutions of the cobalt soaps became a reddish brown and deposited a pink crust mingled with a brown precipitate. It is evident that this method of crystallization might be used to prepare the pure stearates and palmitates. The salts obtained by heating the addition products to constant weight, at a temperature high enough to drive off the pyridine, were found to contain the theoretical proportion of the heavy metal.

From hot solutions of the stearates of lead, chromium, trivalent iron, cadmium, manganese, mercury, and zinc, on cooling or evaporating the solvent, these salts separated out as a sticky amorphous mass. This loses its adherent pyridine and becomes a hard glassy solid like the original salt.

Förster<sup>1</sup> obtained bright green crystalline plates of  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{C}_5\text{H}_5\text{N}$  and deep blue needles of  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{C}_5\text{H}_5\text{N}$  from aqueous solutions of the acetates with pyridine. Grossman and Hünsele<sup>2</sup> obtained dark blue plates of  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ . These crystals in their appearance and composition were analogous to the compounds of the stearates and palmitates of copper with pyridine. Senbert and Rauter<sup>3</sup> describe crystals, of similar appearance and composition, of copper oxalate with pyridine. Grossman and Jäger<sup>4</sup> also describe red crystalline plates of the oxalates, acetates, formates and tartrates of cobalt, each with two molecules of pyridine to a molecule of the salt, and green crystals of nickel acetate with two molecules of pyridine. These are also analogous to the corresponding stearates and palmitates. The last investigators found similar addition products with the acetates and formates of such bivalent metals as manganese, mercury, cadmium, and zinc. Aside from a kind of crystalline crust and spherical nodules, no definite crystalline product with the stearates of these metals was formed. Lutschak<sup>5</sup> gives many analogous addition products of salts of the heavy metals with ammonia.

<sup>1</sup> *Ber.*, 25, 3416 (1892).

<sup>2</sup> *Z. anorg. Chem.*, 46, 301 (1905).

<sup>3</sup> *Ber.*, 25, 2823 (1892).

<sup>4</sup> *Z. anorg. Chem.*, 48, 73 (1906).

<sup>5</sup> *Ber.*, 5, 30 (1872).

Saturated solutions of copper and cobalt stearates in quinoline, amylacetate, and benzaldehyde were prepared at about  $70^{\circ}$  and allowed to cool. The quinoline and benzaldehyde solutions apparently yielded crystals. As there was evident decomposition, shown by the blackening of the solution, these crystals were not investigated further. With amyl acetate the copper stearate swells up to more than four times its original volume and forms light blue granules which contain over half their weight of amylacetate.

The stearates of nickel, cobalt, copper and chromium dissolved readily in melted stearic acid and paraffin. Uniform solids were formed on cooling. Apparently no addition product separated out. With a view to making a double sodium copper salt, the copper stearate was heated for a long time in a concentrated aqueous solution of sodium stearate. The copper stearate remained unchanged. The treatment of the copper soap with an alcoholic solution of sodium stearate resulted in no apparent change in the copper stearate.

To determine the composition of the crystalline addition products, the crystals were formed in crystallizing dishes. The pyridine was drained off, the crystals thrown upon filter paper, and dried as quickly as possible. Portions for analysis were placed in crucibles and weighed. The samples were heated in an air bath at  $115$  to  $120^{\circ}$  to constant weight and the pyridine determined by the loss in weight. The crucibles were then placed on a sand bath and so heated that the organic matter was charred and gradually oxidized. To insure the complete oxidation of the organic radical, the contents of the crucibles were treated with a quantity of finely powdered ammonium nitrate and finally a few drops of nitric acid. The copper and nickel were determined as the oxides. The cobalt was converted into the sulfate and weighed as such. Each of the results given in Table III is the average of two or three analyses.

It has been noted by Kahlenberg that cobalt oleate, dissolved in xylene, changes from pink to blue on heating. A number of such color changes in the solutions of the stearates and palmitates was noted. A solution of cobalt stearate in Merck's paraffin, m. p. about  $60^{\circ}$  was brown when cold. It melted to a straw colored liquid, became pink, and finally was a deep blue at about  $180^{\circ}$ . Cobalt stearate dissolved readily in melted stearic acid, palmitic acid, naphthalene, and phenol. These mixtures behaved in a manner similar to that of the paraffin solution. A dilute solution of the salt in benzene, carbon tetrachloride, or amyl alcohol solidified to a pink jelly which, on heating, melted and changed to lavender color and became a deep violet, when the liquid had reached its boiling point. The higher the boiling point of the solution, the more nearly blue the hot solution became. Cobalt palmitate was found to behave in the

same manner as the stearate in all these solvents. In all cases the solutions became pink on cooling and blue on heating.

TABLE III.—RESULTS OF ANALYSES.  
Blue crystals of copper stearate with pyridine.

	Copper oxide.	Pyridine.
Calc. for $\text{Cu}(\text{C}_{17}\text{H}_{35}\text{COO})_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ .....	10.10%	20.06%
Found.....	9.93%	21.92%

Green crystals of copper stearate with pyridine.

Calc. for $\text{Cu}(\text{C}_{17}\text{H}_{35}\text{COO})_2 \cdot \text{C}_5\text{H}_5\text{N}$ .....	11.14%	11.33%
Found.....	11.21%	11.27%

Green crystals of copper palmitate with pyridine.

Calc. for $\text{Cu}(\text{C}_{16}\text{H}_{31}\text{COO})_2 \cdot \text{C}_5\text{H}_5\text{N}$ .....	12.12%	12.21%
Found.....	11.96%	12.13%

Red crystals of cobalt stearate with pyridine

	Cobalt sulfate.	Pyridine.
Calc. for $\text{Co}(\text{C}_{17}\text{H}_{35}\text{COO})_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ .....	19.86%	20.18%
Found.....	19.96%	20.23%

Red crystals of cobalt palmitate with pyridine.

Calc. for $\text{Co}(\text{C}_{16}\text{H}_{31}\text{COO})_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ .....	21.46%	21.74%
Found.....	21.72%	21.58%

Green crystals of nickel stearate with pyridine.

	Nickel oxide.	Pyridine.
Calc. for $\text{Ni}(\text{C}_{17}\text{H}_{35}\text{COO})_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ .....	10.21%	21.52%
Found.....	10.09%	21.57%

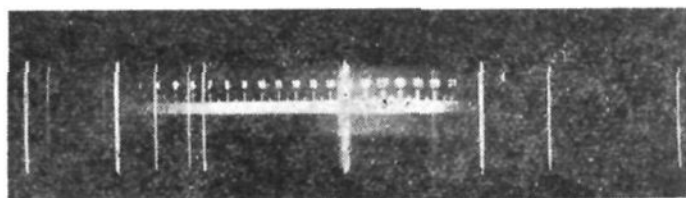
The red crystals of cobalt stearate and palmitate with pyridine melt and change to deep blue on heating to about 150°. On cooling they return to their original red color. The dry cobalt soap itself melted to a rose colored liquid which turned to blue on heating. Even after heating for several minutes over a bunsen flame, the salt would assume its rose color when it had cooled. The color change in these cobalt salts must consequently be due to some intramolecular change and can not be ascribed to hydration or ionization.

Copper stearate dissolved in hot paraffin or naphthalene gave a light yellow solution which formed a bright green solid on cooling to room temperature. The yellow color would return when it was melted and on solidifying the solid would again become bright green. Copper abietate behaves in a similar manner, and it has been noted in this laboratory that copper camphorate also showed this property. These changes are evidently analogous to those of the cobalt salts.

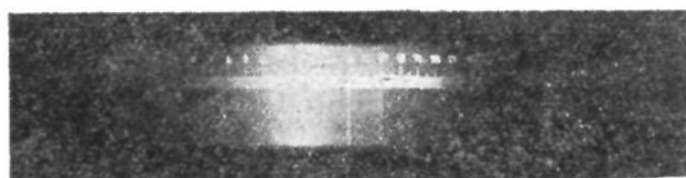
*Absorption Spectra.*—A half or quarter normal solution of the stearate was prepared and placed in a two-millimeter cell. The absorption spectrum of this solution was photographed. Five cubic centimeters of the solution were then diluted with an equal volume of the solvent. The absorption spectrum of this dilute solution was photographed. This



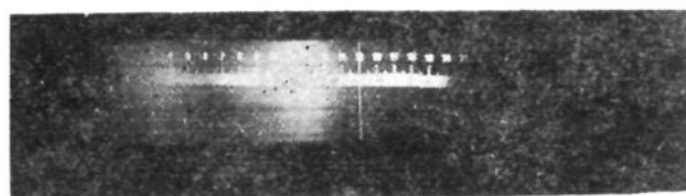
method of procedure was continued until the spectra of six dilutions had been obtained. Thus the photographs of the pyridine and carbon tetrachloride solutions of the stearates of copper, cobalt, and nickel were obtained. These were compared with the photographs of the absorption spectra of aqueous solutions of the chlorides of the same metals made in the same way with the exception that the first solution was four times as strong. This strength was used because it takes an aqueous solution of



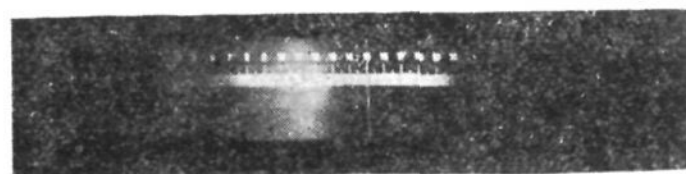
Helium spark spectrum.



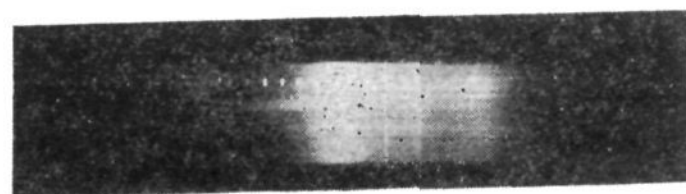
$n$  solution of copper chloride in water.



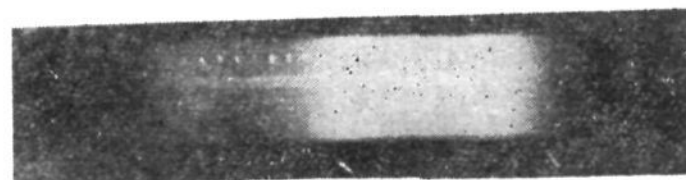
$n/16$  solution of copper stearate in pyridine.



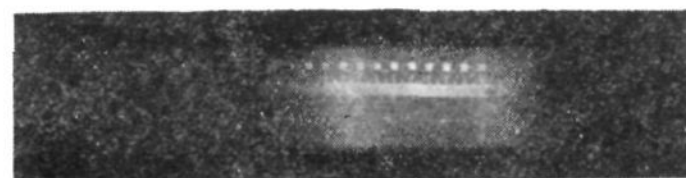
$n/16$  solution of copper stearate in carbon tetrachloride.



$n/2$  solution of nickel chloride in water.



$n/16$  solution of nickel stearate in pyridine.



$n/16$  solution of nickel stearate in carbon tetrachloride.

about four times the concentration of the solution of the soap of the same metal to produce a liquid of the same intensity of color. Upon each spectrum photograph, there were also a scale and the sodium lines. To furnish a scale of reference, this same scale was photographed with the sodium lines and a spark spectrum of helium. The photographs were made by means of a Steinheil spectrometer with a Rowland grating. Cramer's Spectrum Plates were used and each was given the same time of exposure and development.

As far as this work was carried, there appeared no fundamental difference between the absorption spectra of the aqueous solutions of the salts of copper, cobalt, and nickel and those of the solutions of their stearates in non-aqueous solvents. The spectrum photographs have not all been included in this paper. However those given in Plate I, show that the insulating solutions of the salts of copper and nickel have practically the same absorption spectra as the conducting solutions of salts of these metals, and the color of these solutions can not be attributed to the presence of copper and nickel ions.

#### Summary and Conclusions.

1. The copper, cobalt, nickel, ferric, manganese, chromium, and lead stearates and the copper, cobalt, and nickel palmitates have been prepared and described. Stannic stearate was prepared by double decomposition in benzene. A number of such instantaneous double decompositions with the stearates and palmitates in insulating solutions was noted. Such instantaneous precipitations can therefore not be attributed to the unsaturated condition of the acid radical as claimed by Cady.

2. The solubility of the above mentioned salts was determined in pyridine, benzene, toluene, carbon bisulfide, chloroform, carbon tetrachloride, amyl alcohol, methyl alcohol, ether, acetone, ethyl acetate, paraffin, and heptane.

3. A series of crystalline compounds of some of the stearates and palmitates with pyridine was obtained. A number of these compounds have been described and their formulae determined by analysis. These data would be valuable as a means of purifying the stearates and palmitates of the heavy metals. They were also of interest because they fit in a series of analogous crystalline addition products of the salts of other organic acids with nitrogen bases.

4. Cobalt stearate and palmitate, when dissolved in a number of solvents such as paraffin, phenol, naphthalene, and toluene, and even the dry salts themselves, were found to change from pink to blue when they were heated. This would indicate that the change in color which is well known in aqueous solutions of cobalt salts, can not be due to hydration or the presence of ions in the solution, but is probably due to some intramolecular change.

5. The absorption spectra of the aqueous solutions of the chlorides of copper, cobalt, and nickel and of the pyridine and carbon tetrachloride solutions of the stearates of these metals have been photographed. No fundamental difference has been noted in the absorption spectra of the aqueous and non-aqueous solutions.

The author wishes to take this opportunity of thanking Professor Kahlenberg for his valuable suggestions during the progress of this work which was undertaken at his request.

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## THE PREPARATION OF COMPOUNDS OF TRYPAN-RED WITH IODINE AND OTHER SUBSTANCES.

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It was found by Lewis<sup>1</sup> in 1912 in this laboratory that certain dyes, namely, trypan-red, trypan-blue, and isamine-blue, had a more or less selective affinity for different portions of the tuberculous tissue experimentally produced in the rabbit. Trypan-red, for example, when injected into a living animal which was suffering from tuberculosis, would be found after several days in considerable concentration in the central, more or less necrotic portions of the diseased tissues.

It was thought possible that this fact might be used as the basis for an attempt to distribute various physiologically active substances to the diseased tissue. Iodine was the active substance first selected. It was chosen because it is one of the few substances having any sustained reputation among physicians as a useful agent in the treatment of certain forms of localized tuberculosis. It is my purpose to present here, as briefly as possible, the purely chemical aspects of the work so far done. The physiological results obtained with the use of the substances whose preparation and analyses are presented in this paper will shortly be reported in an appropriate place.

The chemical problem, accordingly, was to prepare compounds allied physiologically to trypan-red and containing iodine in the molecule. We have been able to obtain three direct substitution products of trypan-red with iodine. A compound of iodoform and trypan-red has been produced. We were able to obtain compounds of the dyestuff with thymol, eucalyptol, guaiacol, phenol, the cresols, cinnamic esters and pyrrol. The compounds with these substances have been further varied by substitution with iodine.

<sup>1</sup> Paul A. Lewis, "The Selective Relation of Certain Vital Stains to the Tubercle," *Arch. Intern. Med.*, 10, 68 (1912).