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MADISON SQUARE AREA
Report A-2904
TECHNICAL INFORMATION REPORT
For the Period
1 June - 30 June 1945

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Report A-2904

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by Carl Spradlin TISOR, date 9/22/55

TECHNICAL INFORMATION REPORT

For the Period
1 June----30 June 1945

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MADISON SQUARE AREA
MANHATTAN DISTRICT
CORPS OF ENGINEERS

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Report A-2904
Section A

PRODUCTION OF BLACK OXIDE, SODA SALT, ETC.

The following report has been received from the Princeton Analytical Group, Princeton, N.J. Dr. N.H. Furman, Leader.

THE SOLUBILITY OF SODIUM URANYL CARBONATE

by

R.J. Mundy and W.E. Bunce

A request has been made of this laboratory to study the solubility of uranyl carbonate in various concentrations of sodium carbonate, sodium bicarbonate, and carbon dioxide in water at several different temperatures. These studies were to be fundamental in character but the results would be applicable to the problems of neutralizing solutions of uranyl sulfate and the leaching of certain residues.

No information could be found in the literature on the preparation of uranyl carbonate. It appears to exist only in the form of a mineral. Neither the precipitate nor the soluble product that forms on adding sodium carbonate to a solution of uranyl sulfate appears to be uranyl carbonate. Tests made in this laboratory indicate that the precipitate that forms when sodium carbonate is added to a solution of uranyl sulfate is not a definite compound but a mixture of compounds. Several factors, such as temperature, rate of addition of sodium carbonate, and even stirring, appear to have a bearing upon the formation of the precipitate. Carbon dioxide is liberated in the early stages of the neutralization and this fact may account for these erratic results.

On adding sodium carbonate to a solution of uranyl sulfate, a precipitate forms in some cases before one mole of sodium carbonate per mole of uranyl sulfate has been added. In other cases, almost two moles of sodium carbonate per mole of uranyl sulfate must be added before a precipitate occurs. In still other cases, only a slight turbidity occurs after adding over three moles of sodium carbonate per mole of uranyl sulfate. The composition of the precipitate ranges from 68.38 to 75.15 per cent uranium, 4.72 to 6.81 per cent sodium, 0.02 to 5.56 per cent carbon dioxide, and from 0.00 to 12.05 per cent sulfate. Qualitative tests indicate that the precipitate that forms

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on adding sodium carbonate to a solution of uranyl sulfate is not soluble in an excess of sodium carbonate, but is readily soluble in sodium bicarbonate. It has been further found that no precipitate forms if sodium bicarbonate is added to a solution of uranyl sulfate at room temperature, or if an excess of sodium carbonate is rapidly added to such a solution even though no free acid is present. Carbon dioxide is generated in the first stage of the neutralization of uranyl sulfate with sodium carbonate, and, if this can be prevented from being liberated, no precipitate will form. When sodium carbonate is added to a slurry of soda salt, prepared from sodium hydroxide and uranyl sulfate and washed to free it of excess sodium hydroxide and sodium sulfate, only a trace of uranium dissolves after several days at 60°C. This trace of soluble uranium may be brought about by the presence of bicarbonate in the sodium carbonate. An excess of sodium bicarbonate added to a slurry of soda salt, purified as previously mentioned, rapidly dissolves the soda salt at 60°C, producing a supersaturated solution containing about twice as much uranium as that present in a saturated solution. This supersaturated solution approaches the equilibrium state very slowly. Several weeks are required for the liquid to come to equilibrium with the solid that crystallizes.

The soluble product that forms when sodium carbonate is added in excess to a solution of uranyl sulfate is believed to be sodium uranyl carbonate ($2\text{Na}_2\text{CO}_3 \cdot \text{UO}_2\text{CO}_3$). This product was used as the solid phase in the following solubility tests in place of the non-existing uranyl carbonate. It was prepared by dissolving freshly precipitated soda salt in a solution of sodium bicarbonate. The solid tricarbonatate was obtained by evaporating to a low volume while passing carbon dioxide through the solution. A recrystallization was carried out to free the tricarbonatate of any excess bicarbonate that may have been occluded in the first crystallization. The passing of carbon dioxide through the solution during evaporation was necessitated by the fact that decomposition of the tri carbonatate would have otherwise occurred. Apparently the decomposition is brought about by the loss of carbon dioxide from solutions of tricarbonatate on heating. The soda salt was prepared by adding a slight excess of sodium hydroxide to a solution of uranyl sulfate. The sodium sulfate formed in this reaction is exceedingly difficult to remove by filtration and washing. The first batch of tricarbonatate was prepared from soda salt that had been filtered and washed to remove the sulfate. In spite of this washing and a subsequent double crystallization of the tricarbonatate, the final product contained 0.12 per cent sulfate. Further batches of tricarbonatate were prepared from soda salt that had been washed with 0.5 per cent sodium hydroxide solution by decantation until free of sulfate. The sodium hydroxide wash was used to eliminate

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peptization that otherwise would have occurred. The sodium hydroxide left in the slurry after the washing operation was converted to sodium bicarbonate by diluting with water and passing carbon dioxide through the solution.

A large excess of sodium bicarbonate is not required to dissolve the soda salt but the process of dissolving is slow and consumes considerable time. A stoichiometric amount of bicarbonate will dissolve soda salt if the mixture is heated for eight to twelve hours at about 60° to 70°C while a continuous stream of carbon dioxide is passed through the solution.

The solubility tests were first carried out by adding an excess of solid sodium tricarbonates to a solution of the various solvents in wide-mouth, 4-ounce bottles. The bottles were capped with rubber stoppers through which a stirrer driven by a small electric motor was inserted. The solutions were heated in a constant temperature water bath at a definite temperature, and continuously stirred. After a period of time the stirring was stopped and another stopper fitted with a cell containing a sintered glass bottom was inserted. This cell was previously heated to the temperature of the constant temperature water bath. The solution of the soluble tricarbonates was forced into the sampling cell by applying air pressure from a syringe bulb through a second tube in the rubber stopper. Ten ml samples were taken from the sampling cell with a pipette that was preheated to the temperature of the solution. Samples were taken periodically and analyzed for their uranium content.

Sodium uranyl carbonate dissolves at a very slow rate, and considerable time is required to obtain a saturated solution. Approaching saturation from a supersaturated solution is likewise a slow process. Because the rate of solution is a slow process, the advantage of continuous agitation with mechanical stirrers is more than offset by the difficulties encountered in mechanical breakdowns and loss of solution by evaporation. The final solubility tests were carried out in flasks that were capped with rubber stoppers and placed in constant temperature water baths and ovens. The flasks were shaken twice a day and sampled as previously described. In most cases Corning alkali-resistant glass No. 728 had to be used for solutions containing sodium carbonate, for at high temperatures and long periods of time Pyrex glass is readily attacked. Further difficulties were encountered in wiring the rubber stoppers into No. 728 glass flasks. The pressure developed by heating to 90°C was greater than the flasks could stand and several flasks were broken in this manner. This difficulty was eliminated by inserting Bunsen valves in the rubber stoppers used to seal the flasks. The pressure that developed when the flasks containing the sodium carbonate and sodium uranyl carbonate were completely sealed from the atmosphere and

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heated, appeared to be due to water vapor and the expansion of the enclosed air, for no evidence of evolution of carbon dioxide from these solutions could be found. However, solutions of bicarbonate liberate carbon dioxide on heating to 90°C, and, since a pressure of over one and one-half atmospheres developed, the sodium bicarbonate tests at 90°C were considered impractical. At 60°C only a fraction of an atmosphere of pressure developed from solutions of sodium bicarbonate and sodium uranyl carbonate, and these tests were carried out by wiring rubber stoppers into Pyrex flasks containing the above solutions.

Since sodium sulfate is formed when solutions of uranyl sulfate are neutralized with sodium carbonate, tests were made to determine its effect on the solubility of the tricarboxylate. Preliminary results indicated that the sodium sulfate had a marked effect upon the solubility of sodium uranyl carbonate; therefore extensive tests were made to determine the effect of various sulfates, both alone and in conjunction with sodium carbonate and sodium bicarbonate.

The solubility of sodium uranyl carbonate at saturation in the various solvents at 30°, 60°, and 90°C is given in Tables I, II, and III, respectively. The density and pH of the solutions at saturation are likewise given. Some idea of the slow rate of solution of the tricarboxylate is given in Table IV. Figure I shows the variation of the solubility with increasing concentrations of sodium carbonate and sodium bicarbonate at different temperatures.

Several definite trends are indicated by the data. The solubility falls off at a marked rate as the concentration of carbonate is increased. At 2 molar sodium carbonate the solubility is only about five to ten per cent of that of a solution containing no sodium carbonate. As the temperature is increased, the solubility decreases. At 90°C values are obtained that are about one-half to three-fourths of those at 30°C.

A solution of the tricarboxylate in pure water decomposes on heating. The decomposition is slight at 30°C but is marked at 90°C. It appears that sodium carbonate or sodium bicarbonate is generated in the decomposition and concentrates to a point where further decomposition is prevented. No decomposition takes place in concentrations of 0.5 M sodium carbonate or sodium bicarbonate at temperatures between 30° and 90°C.

On a molarity basis, sodium bicarbonate does not suppress the solubility of the tricarboxylate to the extent that sodium carbonate does. However, one molar sodium carbonate becomes two molar sodium bicarbonate if sufficient carbon dioxide is absorbed or added. Since two molar sodium bicarbonate suppresses the solubility of the tricarboxylate to a greater extent than does one molar sodium carbonate, it appears that the absorption of

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carbon dioxide by sodium carbonate solutions brings about a lower solubility, whereas loss of carbon dioxide from sodium bicarbonate solutions brings about a greater solubility.

The presence of sodium sulfate appears to have about the same effect as an equivalent molarity of sodium carbonate in suppressing the solubility of the tricarbonates. Potassium sulfate at 30°C suppresses the solubility to a greater extent than does sodium sulfate. Ammonium sulfate increases the solubility of the tricarbonates to an appreciable extent when present in solutions of bicarbonate or water. This is probably attributable to the formation of ammonium uranyl carbonate, the solubility of which is greater than that of either sodium or potassium tricarbonates. The addition of ammonium sulfate to solutions of uranyl sulfate prior to neutralization with sodium carbonate may be a convenient way of increasing the concentration of dissolved uranium.

Sodium uranyl carbonate appears to be more soluble in solutions saturated with carbon dioxide than in pure water. However, decomposition does not take place in solutions saturated with carbon dioxide and consequently no alkali is generated. This may account for the increase in solubility.

The concentration of sodium uranyl carbonate in the solutions approaching saturation, as well as in those saturated, was determined by acidifying a portion with sulfuric acid, boiling to remove the carbon dioxide, reducing in a Jones reductor, and titrating with ceric sulfate after aeration. The density of the final solutions was determined by weighing a 10 ml sample. The pH was measured with a pH meter, using a special, high-sodium, glass electrode and a standard calomel electrode. The concentration of the various sulfates was determined by precipitation of the sulfate with barium chloride. The concentration of free sodium carbonate and sodium bicarbonate was calculated from a carbon dioxide determination and the known concentration of sodium uranyl carbonate. The amount of carbon dioxide necessary to satisfy the formula $2\text{Na}_2\text{CO}_3 \cdot \text{UO}_2\text{CO}_3$ was calculated and subtracted from the total carbon dioxide, the difference being considered present as either sodium carbonate or sodium bicarbonate. Sodium was determined on two of the sodium bicarbonate solutions in the 60°C series, and it was found that approximately ten per cent of the excess carbonate was present as sodium carbonate. This apparently was due to the escape of carbon dioxide when the flasks were opened to obtain samples. The error introduced by considering all of the carbonate present as sodium bicarbonate is slight.

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The loss of carbon dioxide from this source in the 30°C series was considered negligible, and was not determined. Carbon dioxide was determined by acidifying a portion of the tricarbonat liquor and collecting the carbon dioxide on "Ascarite". Sodium was determined as the sulfate by removing the uranium with ammonia, and evaporating the solution to dryness with sulfuric acid. The solid phase remaining at saturation was analyzed and found to correspond to $2\text{Na}_2\text{CO}_3 \cdot \text{UO}_2\text{CO}_3$.

Table I

Solubility of Sodium Uranyl Carbonate at 30°C

<u>Solvent</u>	<u>Solubility expressed as grams of $2\text{Na}_2\text{CO}_3 \cdot \text{UO}_2\text{CO}_3$ contained in 100 ml of solvent</u>	<u>Solubility expressed as grams of U_3O_8 contained in 100 ml of solvent</u>	<u>Density of saturated solution</u>	<u>pH of saturated solution</u>
Water	14.38	7.45	1.118	8.78
0.51 M Na_2CO_3	7.36	3.81	1.106	10.99
1.03 M Na_2CO_3	3.72	1.93	1.128	11.28
2.11 M Na_2CO_3	1.23	0.64	1.202	11.40
3.24 M Na_2CO_3	0.33	0.17	1.278	11.60
0.41 M NaHCO_3	8.83	4.57	1.098	8.72
0.83 M NaHCO_3	5.08	2.63	1.092	8.25
1.05 M NaHCO_3	4.13	2.14	1.100	8.32
0.50 M Na_2SO_4	6.45	3.34	1.110	8.78
0.50 M Na_2SO_4	3.98	2.06	1.138	11.00
0.51 M Na_2CO_3				
0.50 M Na_2SO_4	4.53	2.35	1.120	8.17
0.42 M NaHCO_3				
0.51 M K_2SO_4	4.09	2.12	1.094	8.78
0.51 M K_2SO_4	2.82	1.46	1.111	8.18
0.41 M NaHCO_3				
0.48 M $(\text{NH}_4)_2\text{CO}_3$	20.01	10.36	1.201	8.47
0.48 M $(\text{NH}_4)_2\text{CO}_3$	17.20	8.91	1.197	8.05
0.35 M NaHCO_3				
Water saturated with CO_2	15.20	7.87	1.123	6.85

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Table II

Solubility of Sodium Uranyl Carbonate at 60°C

<u>Solvent</u>	<u>Solubility expressed as grams of 2Na₂CO₃.UO₂CO₃ contained in '100 ml of solvent</u>	<u>Solubility expressed as grams of U₃O₈ contained in 100 ml of solvent</u>	<u>Density of saturated solution</u>	<u>pH of saturated solution</u>
Water *	12.31	6.38	1.094	8.72
0.52 M Na ₂ CO ₃	4.81	2.49	1.079	11.22
1.05 M Na ₂ CO ₃	2.15	1.11	1.106	11.31
2.12 M Na ₂ CO ₃	0.66	0.34	1.187	11.58
3.31 M Na ₂ CO ₃	0.19	0.10	1.278	11.68
0.43 M NaHCO ₃	6.56	3.40	1.070	8.32
0.05 M Na ₂ CO ₃	3.46	1.79	1.062	8.38
0.68 M NaHCO ₃	1.86	0.96	1.076	8.32
1.47 M NaHCO ₃	1.38	0.71	1.099	8.50
1.64 M NaHCO ₃	1.38	0.71	1.099	8.50
0.18 M Na ₂ CO ₃	5.02	2.60	1.092	8.50
0.51 M Na ₂ SO ₄	2.34	1.21	1.113	11.12
0.50 M Na ₂ SO ₄	2.80	1.45	1.098	8.32
0.48 M NaHCO ₃	4.58	2.37	1.091	8.86
0.50 M K ₂ SO ₄	2.90	1.50	1.124	11.27
0.52 M NaCO ₃	3.30	1.71	1.106	8.38
0.49 M K ₂ SO ₄				
0.48 M NaHCO ₃				
Water saturated with CO ₂	12.85	6.65		

* 0.02 M Na₂CO₃ and 0.02 M NaHCO₃ present due to decomposition.

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Table III

Solubility of Sodium Uranyl Carbonate at 90°C

<u>Solvent</u>	<u>Solubility expressed as grams of 2Na₂CO₃·UO₂CO₃ contained in 100 ml of solvent</u>	<u>Solubility expressed as grams of U₃O₈ contained in 100 ml of solvent</u>	<u>Density of saturated solution</u>	<u>pH of saturated solution</u>
Water *	10.17	5.26	1.074	8.78
0.53 M Na ₂ CO ₃	3.56	1.84	1.059	10.82
1.02 M Na ₂ CO ₃	2.11	1.09	1.095	10.99
2.13 M Na ₂ CO ₃	0.47	0.24	1.175	11.28
3.37 M Na ₂ CO ₃	0.17	0.09	1.259	11.32
0.52 M Na ₂ SO ₄	3.44	1.78	1.047	9.10
0.51 M Na ₂ SO ₄	1.51	0.78	1.096	10.72
0.53 M Na ₂ CO ₃				
Water saturated with CO ₂	11.56	5.99	1.081	7.12

* 0.02 M Na₂CO₃ and 0.04 M NaHCO₃ present due to decomposition.

Table IV

Time Required to Reach Saturation, Shaking Flasks Twice a Day

Pure water solution at 30°C - 136 days
Pure water solution at 60°C - 21 days
Pure water solution at 90°C - 17 days

After 7 days the pure water solution at 30°C was about 40% saturated.
After 4 days the pure water solution at 60°C was about 90% saturated.
After 4 days the pure water solution at 90°C was about 100% saturated.

Even with rapid stirring by motor, nearly two days are required to reach 80 per cent saturation in pure water solutions at 30°C. Solutions of 1.0, 2.0, and 3.0 molar sodium carbonate are progressively at a higher per cent of saturation for a given period of time, but all solutions appear to require the same period of time to reach full saturation.

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FIGURE I

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Section E

PRODUCTION OF FINISHED METAL

1. The following report has been received from the Electro Metallurgical Company.

Two attempts were made to cast 1.5 inch diameter rods by the bottom pour method. In each case the mold consisted of four 1.5-inch I.D. by 19 inches long graphite tubes grouped about a center tube of the same dimensions. The bottom of each of the outside tubes was connected to the bottom of the center tube by a one-half inch wide sprue. In the first attempt, the metal was poured into the center tube at a temperature of 1350°C. Five rods were obtained. The four outside rods were only ten inches long but the center rod was 19 inches long. The surface of all rods was good.

In the second pour, the same type of mold was used except that the shape of the sprues was modified to give a better flow of metal. Five rods were also obtained from this heat. However, as in the first pour, all of the rods were not full length. Three of the outside rods were 17 inches long, the fourth was ten inches long, while the center rod was 19 inches long. The surface of all of the rods was very good.

It was concluded from this experiment that at least five single-length rods (9 inches long) can be made simultaneously by the bottom pour method without difficulty. However, to utilize the present capacity of our furnaces it is necessary that such rods be made double-length. There is a good possibility that by limiting the bottom pour set-up to three outside molds, instead of four, and one center mold, four satisfactory double-length rods could be obtained. Then, by casting four such groups with the use of the turntable type furnace bottom, full utilization of furnace capacity could be made.

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2. The following report has been received from Dr. J.G. Thompson, Metallurgical Laboratory, National Bureau of Standards, Washington, D. C.
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Casting of bars in the top-pour, tilting furnace has been shifted to a two-bar basis, i.e., bars are cast in pairs instead of singly as heretofore. No particular difficulty was encountered in casting two bars simultaneously, and the quality appears to be as good as that of singly cast bars. A graphite distributor head is used, with an orifice one-half inch in diameter leading to each of the twin molds. Cast iron molds have been used because of shortage of steel molds, and two of these cast iron molds are still in good condition after 25 bars have been cast in each. The burner method of resmoking was used with these molds until a shortage of molds developed, when a return was made to the old method of smoking by burning benzene on a rag. The latter method gives a heavy and more reliable coating of smoke.

A leak in the vacuum system of the tilting furnace finally was located in the sylphon-type tubing which provides the necessary flexible connection from the furnace to the vacuum line. This is the first difficulty encountered in the vacuum connections of this furnace in more than two years' operation.

Results obtained from the bottom-pour furnace, casting single bars, have improved since it was found that the guide tube in the bottom plate of the furnace was not truly at right angles to the bottom of the furnace. This tipped the mold slightly and brought the top off-center, resulting in splashing of the metal when poured and a tendency to impinge on the side of the mold. After the alignment of the mold was corrected, very satisfactory results were obtained in single-bar casting. The surfaces of the bars are consistently good, at least equal to bars produced in the top-pour furnace, and some bars are superior to the best produced in the top-pour furnace. This probably results from the fact that the metal in the bottom-pour furnace is free from slag and dross, whereas metal poured from the top of the melt, with inadequate skimming, probably is contaminated with dross from time to time.

Molds for the bottom-pour furnace are smoked hot by the burner method. Present indications are that a single smoking results in a heavier deposition of soot at the top end of the mold. Consequently a more uniform coating is obtained by smoking for two-minute, and then inverting the mold for an additional two minutes smoke, rather than a four-minute smoking without inverting the mold.

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Additional measurements of warpage of the cast bars have been made using feeler gages. Observed warpage values ranged from 0.012 to 0.047 inch with a mean value for 87 bars of 0.023 inch. Evidently warpage of the bars as cast ordinarily does not exceed the shrinkage of the bar, i.e., about 0.04 inch.

Investment molds for two-pound ingots were prepared by tamping investment material moistened with 5, 10, and 20 per cent by weight of liquid binder, to investigate the possibilities of using investment material like ordinary foundry sand, i.e., using only enough binder to hold the rammed mold together while the casting is made and having the sand available for re-use with additional small amounts of binder. Molds made with 10 and 20 per cent of binder yielded good castings, but the used mold did not crush as easily as was desired. On the other hand, five per cent of binder was not enough to hold the mold together properly while the casting was made. The results indicate that less than ten per cent of binder must be used if the investment is to be re-used, but more than five per cent of binder is necessary to obtain satisfactory cohesion of the mold and consequent good surface on the casting. An attempt was made to form a twenty-inch mold of seven per cent-bonded material, but difficulty was encountered, apparently because of setting of the binder during the tamping operation. Further attempts to prepare twenty-inch molds are in progress, including a study of the possibility of using ground flint instead of the much more expensive investment material.

There are on hand, for shipment as desired, 85 bars, each 18 inches long. The supply of good melting stock on hand is sufficient to raise this number to about 100. As soon as the casting program is completed, several of the recently cast bars from both furnaces will be subjected to machining tests and inspected for internal defects.

An informal report has been received of the results of the inspection of the first 20 bars, 18 inches long, cast at the National Bureau of Standards. These bars were cast under a variety of experimental conditions which affected the quality of the bars, and were rated very good, good, fair, bad, and very bad, according to their surface appearance. The inspection was to determine the existence of defects larger or deeper than 1/32 inch in the surface, sub-surface, and interior. Step-wise machining tests on ten bars showed that the sub-surface defects were directly related to the appearance of the as-cast surface. A bar rated "very good" cleaned up satisfactorily at a diameter of 1.47 inches after removing only 0.050 inch of metal from the diameter; six bars, rated "good" or "fair", cleaned up after removing 0.075 inch to 0.125 inch of metal, i.e., at diameters between 1.40 inches and 1.45 inches; of three bars rated "bad" or "very bad", two

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cleaned up at 1.360 inches and the third still had one over-size defect in the surface at 1.360 inches diameter. In seven bars which were sectioned longitudinally, only one interior void as large as 1/32 inch was found.

The results indicate that even these early experimental bars were, in general, satisfactory. The fact of the visible improvement in quality of the bars with added experience and the improved procedure in casting leads to the belief that even more satisfactory results would have been obtained if the inspection had been applied to currently produced bars.

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3. The following report has been received from the Mallinckrodt Chemical Works, St. Louis, Mo.

A REPORT ON THE CASTING OF A FOURTH EGG
AND RELATED SUBJECTS

by

W.A. Oppold

Object

To try to find an answer to the problem of pyrophoricity by testing chemically and physically an egg cast from the last material in the crucible.

Summary and Conclusions

- (1) ³ The last metal (in the crucible) as represented by a fourth egg is very high in impurities and gives a high TDS result.
- (2) All the number ^{11, 4} four egg samples were extremely pyrophoric, while the number ^{11, 4} three egg samples were all right with the exception of a few which showed a tendency to be pyrophoric.
- (3) A literature search showed that phosphides and sulfides of uranium are pyrophoric, and it is possible that both these compounds could be present in the finished metal in such quantities as to cause pyrophoricity.
- (4) A report from Chicago on the metallographic examination of pyrophoric and non-pyrophoric samples of metal states the following conclusions as a result of their investigations:
"Microscopic porosity would seem to be the cause of the pyrophoric condition."

Discussion

It has been known for some time that the metal in the last part of the pour from a remelt furnace is much higher in impurities than the first metal out of the crucible. This could be explained by the fact that the impurities and slag are lighter than the metal and tend to concentrate at the top of the melt. After the metal melts, it is agitated violently by its own boiling. This tends to drive the impurities out of the main body of the melt and to the top of the crucible. Therefore, when the pour is made,

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most of the impurities come out of the crucible last and go into the third billet. It also follows that the top of the third billet would be higher in impurities than the bottom of the same billet. Chemical analyses on samples cut from the three billets from time to time have shown this to be true.

Since some chemical impurities are probably the cause of pyrophoricity, the number 3 billet should have a higher percentage of pyrophoric material than the other two billets. This has been the case, as results from the extrusion operation show that 75 to 80 per cent of the billets that were pyrophoric were number 3 ingots.

Arrangements were made with Chicago to run the TDS test on piles of eggs from all number one, all number two, and all number 3 billets, respectively. To make the results more complete, it was decided to cast a fourth egg from the last metal in the crucible. This was done as follows. The fourth or "drip" mold was used for casting the egg. Five extra pounds of metal were added to the regular charge to insure leaving enough metal for the fourth egg. The three billets were poured into the drip mold. When the furnace was unloaded and there was enough solid metal in the drip mold, an egg was cut from it and marked with the three K numbers of the billets in that heat. Then the 16 number one, 16 number two, 16 number three, and the 16 number four eggs were piled and the TDS test was run on them. The results are listed below.

<u>Egg Number</u>	<u>TDS</u>
One	0.14
Two	0.14
Three	0.14
Four	0.80

As can be seen, the TDS for the fourth egg was much higher than that for the other sets of eggs. Since the TDS test is statistical, a great number of runs would be necessary to get accurate results, but as an order of magnitude answer was sufficient, one run was enough to give a suitable result. Probably over a period of time, the TDS results would be lowest on the number one eggs, becoming higher on two and three, and much higher for the fourth egg.

After the candling tests were completed, the number 3 and 4 eggs were sent back to the Mallinckrodt Chemical Works for analysis and testing. A 1/8-inch slice was cut from each of the eggs. This slice was then sawed in two. One-half was used for the pyrophoricity test. The other half of the slice from the number 4 eggs was tested chemically for manganese, magnesium, nitrogen, silicon, chloride, carbon, hydrogen, and iron, and for density. Chemical results had already been obtained on the third eggs, so no more work was done on these samples.

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The pyrophoricity tests were run as described below.

A muffle was set up so that argon gas could be run through a stainless steel coffin containing the samples. The muffle was heated to 1650°F and the samples were put in fused quartz trays to facilitate their entry to and removal from the hot coffin.

Procedure used to run samples

The muffle was turned on and allowed to get to 1650°F and then it was kept there for one hour before the tests were started. The argon cylinder was connected to the inlet pipe of the coffin and the interior of the coffin was well flushed with the gas. The outlet from the coffin was connected to a piece of rubber hose which was immersed in water. This acted as a bubbler and was a means of keeping the flow of gas constant. As soon as the coffin was flushed out well, the door was removed and the quartz dish containing the sample was inserted. The door was then closed and bolted on, and a steady flow of argon gas was run through the coffin. The sample was left in the muffle for fifteen minutes, by which time it had been at 1650°F for about five minutes. The door to the coffin was removed and the dish and sample were taken out of the furnace and cooled in air. From the behavior of the sample during this cooling in air, its pyrophoricity was estimated.

The results are listed in Table I. Column one gives the K numbers of the eggs tested. Column two shows the pour position of the egg. Column three gives the results of the pyrophoricity test.

Table I

<u>K Number</u>	<u>Position</u>	<u>Remarks</u>
9906	No. 3	O.K. to Fair
9909	No. 3	O.K.
9919	No. 3	O.K.
9924	No. 3	O.K.
9930	No. 3	O.K.
9933	No. 3	O.K.
9945	No. 3	O.K.
9948	No. 3	O.K.

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Table I (Cont'd)

<u>K Number</u>	<u>Position</u>	<u>Remarks</u>
9951	No. 3	Poor to pyrophoric
9954	No. 3	Poor to pyrophoric
9957	No. 3	Poor to pyrophoric
9960	No. 3	O.K.
9964	No. 3	O.K.
9970	No. 3	O.K. to Fair
9973	No. 3	O.K. to Fair
9976	No. 3	O.K.
9904-05-06	No. 4	Pyrophoric
9907-08-09	No. 4	Pyrophoric
9917-18-19	No. 4	Pyrophoric
9922-23-24	No. 4	Pyrophoric
9928-24-30	No. 4	Pyrophoric
9931-32-33	No. 4	Pyrophoric
9943-44-45	No. 4	Pyrophoric
9946-47-48	No. 4	Pyrophoric
9949-50-51	No. 4	Pyrophoric
9952-53-54	No. 4	Pyrophoric
9955-56-57	No. 4	Pyrophoric
9958-59-60	No. 4	Pyrophoric
9962-63-64	No. 4	Pyrophoric
9968-69-70	No. 4	Pyrophoric
9971-72-73	No. 4	Pyrophoric
9974-75-76	No. 4	Pyrophoric

As can be seen from the table, all the slices from the number 4 eggs were pyrophoric. These samples all turned to black oxide with some sparking. Most of the number 3 samples were all right with the exception of six slices which showed some tendencies to become pyrophoric. These six samples were not nearly as bad as the fourth egg samples.

The chemical analyses of the third and fourth eggs are listed in Tables II and III. The analyses for the number three eggs (Table II) show nothing unusual with the exception of billet number 9970, which was high in nitrogen. This sample was not pyrophoric, but showed some tendency to be so. Some of the magnesium analyses were a little high but nothing out of the ordinary.

Table III shows the chemical analyses of the fourth egg. The results on silver, chromium, nickel, boron and iron were not different from the third egg analyses. Some of the samples, when dissolved for the nitrogen test, gave off phosphine. Also, when a sample was burned for the

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carbon-hydrogen analyses, a yellow speck was noticed which, when tested, was found to be phosphorus. Most of the samples were then tested for phosphorus, but the results were all low, as can be seen in column six of Table III. Therefore, if there is phosphorus in the metal in large amounts, it must be segregated and a sample cut from a slice of metal might not include it.

Column 7 shows a few cobalt analyses around the 10 ppm range, which is a little higher than usual. The manganese analyses in column 8 are not consistently higher than the third egg analyses, and none of them are very bad. The magnesium analyses in column 9 are all very high, as are the nitrogen results in column ten. The density results were very low, as can be seen from column eleven. This is partially due to the fact that the number 4 eggs were not too solid and there were small pits in the density samples. Density tests run on the whole egg would probably give better results. The carbon and hydrogen results were also quite a bit higher than the run of good metal, as can be seen from columns twelve and thirteen. Only a few chloride determinations were run, and they were consistent with regular metal analyses. The silica results were a little lower, if anything, than the regular run of material. Some of the silica analyses were obtained by compositing samples, and the rest were run individually.

When some phosphorus was found in the metal, a search was made of the available literature to see if the phosphide of uranium is pyrophoric. There was very little material at hand on this subject, but several references were found in "Researches on Uranous Compounds" by M.A. Colani, Annales de Chimie et de Physique, (8), 12 (1907), pp. 59-144. This article states that uranium phosphide (U_3P_4) burns when heated in air. It was also stated in this article that uranium sulfide (US_2) burns brilliantly when heated in air, and sparks when thrown into a flame. There could be some uranium sulfide present, as there is sulfate in the liner and it is conceivable that this could be carried over into the finished material. The article also states that the selenide of uranium is pyrophoric, but there is no evidence of selenium in the finished metal. Tests are being run to see how much sulfur is present.

Some results on metallographic examinations of pyrophoric and non-pyrophoric material have been received from Chicago. The conclusions from their work are listed below.

- 1) "It is not likely that the relatively small differences in purity of these sets of samples would be the direct cause of marked differences in pyrophoricity."
- 2) "Microscopic porosity would seem to be the cause of the pyrophoric condition."

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Table II

<u>K</u> <u>Number</u> <u>of 3rd</u> <u>egg</u>	<u>Ag</u>	<u>Cr</u>	<u>Ni</u>	<u>Boron</u>	<u>N</u>	<u>Density</u>	<u>Fe</u>	<u>Mn</u>	<u>Mg</u>	<u>Lot</u>
9906	L2.0	L10	L10	L0.2	68	18.93	26	5.8	15.0	EC39
9909					59	18.95	24	4.5	L 2.0	EC39
9919					60	18.94	32	6.2	14.0	EC39
9924					50	18.95	28	6.5	6.6	EC40
9930					65	18.93	17	4.1	16.0	EC40
9933					49	18.93	21	5.3	19.0	EC40
9945					37	18.96	30	-	5.7	EE41
9948					46	18.96	34	-	13.0	EE41
9951					42	18.93	30	6.5	9.0	EG42
9954					56	18.92	29	7.4	24.0	EG42
9957					50	18.93	27	6.4	M30.0	EG42
9960					79	18.89	27	7.9	M30.0	EG42
9964					58	18.95	45	7.5	3.5	EG42
9970					134	18.92	22	7.0	M30.0	EG43
9973					57	18.90	27	6.5	20.0	EG43
9976					51	18.91	33	6.5	M30.0	EG43

All results are listed in ppm
M equals more than
L equals less than

Lot composites are listed below.

<u>Lot Number</u>	<u>Carbon</u>	<u>Hydrogen</u>	<u>Chloride</u>	<u>Silica</u>
EC39	310	7.0	5	50
EC40	420	5.7	5	36
EE41	380	5.3	6	34
EG42	390	5.4	5	40
EG43	480	4.2	5	26

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Table III

<u>K Numbers of 4th egg</u>	<u>Ag</u>	<u>Cr</u>	<u>Ni</u>	<u>B</u>	<u>P</u>	<u>Co</u>	<u>Fe</u>	<u>Mn</u>	<u>Mg</u>	<u>N</u>	<u>Density</u>	<u>Car- bon</u>	<u>Hydro- gen</u>	<u>Cl</u>	<u>Silica</u>
9904-5-6	L2	L10	L10	LO.2	15	L10	31	8.6	850	520	18.27	1260	19.6	--	10*
9907-8-9					7	L10	19	4.2	370	440	18.50	1050	11.2	--	10*
9917-18-19					14	L10	27	7.5	850	885	18.06	2760	10.9	--	10*
9922-23-24					8	10	27	7.7	950	885	18.00	1420	13.0	--	26*
9928-29-30					9	L10	26	7.2	420	510	18.38	860	6.7	--	26*
9931-32-33					-	L10	21	6.1	800	640	18.14	1100	13.6	9	21
9943-44-45					8	L10	24	8.9	800	1230	17.88	1280	20.2	--	26*
9946-47-48					11	10	27	7.8	800	1320	18.17	1310	16.5	--	26*
9949-50-51					8	10	11	3.0	605	1195	17.89	1380	30.4	--	16*
9952-53-54					8	10	17	5.8	1200	820	17.50	820	17.6	--	10*
9955-56-57					6	L10	33	5.8	950	825	17.69	870	15.3	--	16*
9958-59-60					-	L10	10	3.3	740	900	18.36	1140	11.6	5	25
9962-63-64					-	10	16	4.6	700	550	18.45	1080	14.7	12	22
9968-69-70					-	10	10	3.7	645	640	18.57	960	14.9	--	16*
9971-72-73					9	10	13	4.7	950	1140	18.16	1480	18.9	--	16*
9974-75-76					5	L10	17	4.7	850	1500	17.95	1220	12.0	--	10*

All results in ppm
* 3 composite samples

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4. The following is extracted from a progress report of the USEO, Iowa Area, dated 22 June 1945.

- 1) In developing the technique for casting hot dogs at Iowa State College, the ultimate aim has been to produce dogs entirely of pits, inclusions, gas holes, cracks, and internal pipes. To arrive at this objective, first, the metal to be cast must be clean and free from dissolved gas, and second, the rate of pour, the pouring temperature, and the rate and manner of cooling must be determined and controlled. These last three variables depend directly upon the mold design including the method of feeding the metal into the mold, the mold dressing, and the pouring temperature.
- 2) The present air-cooled, top-poured steel mold assembly was designed after considerable experimentation. The steel molds are of seamless tubing, 30 inches long, $1\frac{1}{2}$ -inch I.D., and 3 inches O.D. The assembly consists of nine molds, one in the center and eight around the perimeter. Several methods of feeding the metal into the molds have been tried, such as filling each mold separately, in pairs, in threes, and all simultaneously. The latter was the only method that did not produce one or more cold-pour dogs. This feeder is a plate of graphite 12-inches in diameter and 2 inches thick. The molds are held in position by inserting them into 3-inch holes drilled to a depth of one-inch in the bottom of the feeder plate. One and one-half inch holes are drilled into the top of the feeder plate concentrically with the 3-inch holes, and graphite inserts are pressed into these holes so that the bottom of the inserts are flush with the top of the molds when assembled. The rate of pour is determined by the diameter of the orifice drilled through the inserts, and this rate has been varied by using $\frac{3}{8}$ -inch to $1\frac{1}{2}$ -inch orifices. A seven-sixteenths-inch orifice has been found to give the optimum rate of pour.
- 3) Mold dressings of magnesia, titanium oxide, zinc oxide, Aquadag, and benzene smoke have been investigated. The latter proved to be definitely the best; the first two are unsuitable. Zinc oxide, which is applied in suspension in water and dried, causes subsurface gas bubbles, probably hydrogen, and Aquadag appears to break down below the temperature at which the metal is poured. No dressing was used at all on several runs, but all dogs so cast had deep pipes.
- 4) The pouring temperature has been varied from 1175° to 1260°C, but to obtain best results, we heat to 1350°, cool to 1275°C, and pour.

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- 5) It is pointed out that the casting technique found from the investigations discussed in paragraphs 2, 3, and 4 above is the best developed to date but will undoubtedly change upon further experimentation. The following is a summary of the standard casting procedure.
- a. Use a 2-inch valve in the crucible and 7/16-inch orifices in the feeder inserts.
 - b. Fill all the molds simultaneously.
 - c. Use benzene smoke for a mold dressing. The smoking procedure is to soak 20 cc of benzene on two double sheets of Kleenex, smoke the mold top end down for $1\frac{1}{4}$ minutes, turn the mold right end up until burning is completed, then blow off all loose feathers with compressed air.
 - d. Heat to 1325°C and pour at 1275°C.
- 6) On or about 12 May 1945, the contractor began producing his quota of dogs for ultimate shipment to H.E.W. At about the time 200 individual dogs had been cast, MSA, through this office, requested the contractor to set up a rigid inspection procedure in order to determine that the dogs to be shipped would, for the most part, pass inspection at H.E.W. It was therefore decided that all dogs so far produced should either be machined for surface inspection or cut into $1\frac{1}{2}$ -inch slices for internal pipe inspection. It was also decided that further experimentation would be advisable, particularly since Metal Hydrides would not complete their quota for some time. To date over 600 individual dogs, or approximately 30 runs, have been rigidly inspected and records have been maintained on the results of each experiment.
- 7) Internal pipes or voids appeared to be the greatest obstacle to overcome. Most of these voids are from microscopic size to the width of a pin point, and vary from 1/64 to 1/8-inch long. They are found in the bottom and the bottom half of the middle dog. It is understood that these voids have no deleterious effect if they are enclosed, but it is not certain whether a dog will pass inspection if a void happens to be exposed. These voids are probably due to a non-progressive cooling from bottom to top. Apparently at certain levels the metal freezes from above leaving molten metal below, and when the latter freezes it contracts, and since there is no molten metal above to fill this space a void is formed. Most of the experimentation in the past few weeks has been directed toward eliminating voids by improving the smoking technique to obtain a heavier coating and therefore a more insulating coating progressively to the top of the mold.

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Casting technique has improved during the past two months to the extent that estimated rejections have decreased from fifty per cent to twenty-five per cent. Voids account for one-half of the rejections, while all other defects account for the balance. The causes and remedial steps taken to eliminate the other common defects are discussed below:

- (a) Inclusions are mostly either oxide or carbide. Oxide inclusions were formerly introduced by using brown oxide as a filler around the crucible valve. Zirconium oxide painted on the valve has been found to be successful as a substitute for the brown oxide since it is as effective without causing inclusions. Numerous inclusions resulted when croppings from cast turnings were used for the casting charge. Inclusions of carbon often occurred when the mold smoke was applied to an excess thus forming loose feathers. These inclusions can be kept to a minimum by blowing the feathers off with compressed air.
- (b) Porosity, or a small area containing numerous small black pits, usually occurs when the molten metal strikes the side of the mold. Small particles of carbon that are washed off the mold actually become small sub-surface inclusions, but to the naked eye appear to be porosity. The length and the small cross-section of the mold present a difficult problem in tolerance, both in regard to machining the feeder plate and the inserts, and then in assembling the various components. It was thought that if the turbulence of the metal as it pours through the orifice could be kept to a minimum, there would be less tendency of the metal to hit the side of the mold. To accomplish this, each orifice is bevelled 45° at the top to form a funnel. The graphite wall of the insert is machined to a thin section at the bottom, enabling the molten metal to drop freely into the mold. In spite of all the precautions taken, there is still too much evidence of metal splashing against the mold walls. One definite remedy is to find a mold wash that will resist these conditions.
- (c) Cracks were quite prevalent before the adoption of inserts. Previously it was the practice to drill the orifices through the feeder plate. This made it impossible to have a flush fit between the graphite and the top of the mold. As a result, molten metal would flow into this space, and, upon freezing, would cause stress cracks in the top dog. As mentioned in paragraph 2, the inserts are pressed into $1\frac{1}{2}$ -inch holes in the feeder plate to such a depth that they are flush with the top of the mold.

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- 8) At the present time there are approximately 200 dogs ready for shipment and it is estimated the balance will be completed during the first or second week in July. Each rod, or triple-length dog, is inspected in the following manner. The top three inches are machined to 1.36 inch and the two inches below this are machined to 1.40 inch. From experience it has been found that the top of the dog generally contains the majority of pits, gas holes, and inclusions. If any serious defect shows up from this inspection, the top three inches are cropped off and the three dogs are assumed to be passable. In addition to this, the top dog from the center mold is machined in steps to a final diameter of one inch. This particular dog is generally the poorest of the lot, and by noting the type and size of defects in this dog at various depths a fairly accurate picture of the quality of the remaining dogs is obtained.

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