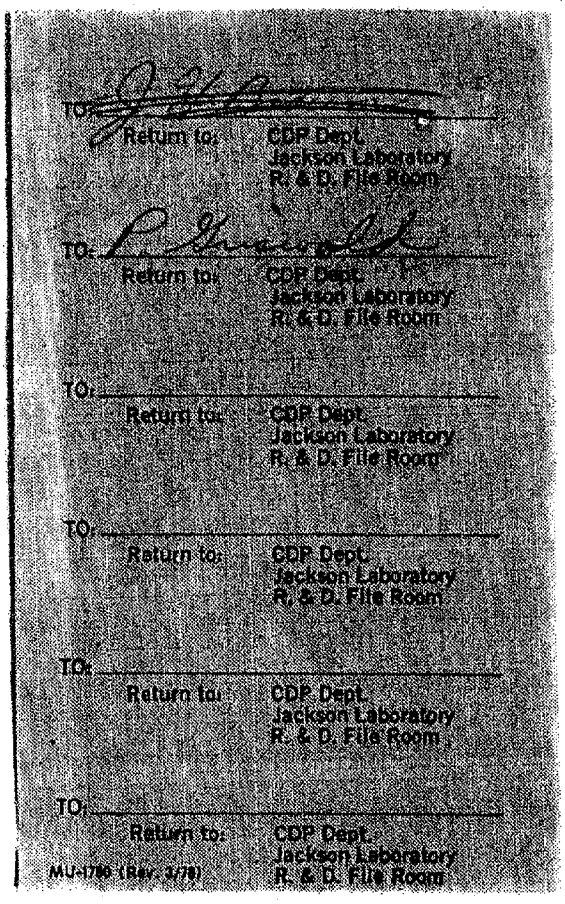

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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

Final Report

EXAMINATION OF LEAD BEARING RESIDUES FOR CONVERSION TO LEAD NITRATE

Period Covered NOVEMBER 7, 1951 - DECEMBER1, 1951

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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

Final Report

EXAMINATION OF LEAD BEARING RESIDUES FOR CONVERSION TO LEAD NITRATE

NOVEMBER 7, 1951 - DECEMBER 1, 1951

Charge: 1101-31-3 (BCN-31-3)

SUBMITTED BY: Julius Jackson JULIUS JACKSON DATE SUBMITTED: 12/7/51

APPROVED BY : B. H. PERKINS 12/14/51 DATE ISSUED: 12/14/51

INTRODUCTION

This report summarizes work on substitutes for corroding grade pig lead. Part of the work was carried out in conjunction with the Quality Control Group who have been working on the general program of pig lead substitutes for some time. The materials examined during the course of this work were:

1. Lead Flue dusts from Bers Smelting and Refining Co., Philadelphia, Pa.

   a. combined flue dusts
   b. reverberatory flue dust

2. Electrotype residues from Essex Metals Co., Newark, N. J. OU 1872 6/11/51

SUMMARY AND CONCLUSIONS

1. Lead nitrate solutions have been made from Bers Reverboratory flue dust, or combined flue dusts, which have the following characteristics:

   a. Excessively high chloride ion content (in excess of 50 parts /1,000,000) despite the fact that residues had been washed with water prior to nitric acid attack. See letter attached - L. B. Magruder, Jr.

   b. The lead nitrate (N-41) solutions require modifications of the standard Y-469-D process (omission of halogens, increased heat development period) to make laboratory preparations of reasonably good quality Y-469-D possible.

   c. Examination of N-41 solutions from Bers dusts have shown the following impurities:

      (1) Cl^- (51-1672) (51-1676, 1677)
      (2) Minor amounts of Mg, Zn, Ca, Cd, Na (51-1676)
      (3) Minor amounts of Na, Ca, Zn, Mg (51-1677)

2. The maximum extent of conversion from dust to soluble lead nitrate under practical conditions has been in the order of 20% of the total nitric acid soluble lead reported in the sample.

3. These data indicate that Bers Reverboratory sludge or combined sludge is not a suitable raw material for the manufacture of lead nitrate by a process analogous to the one presently in use by the plant. The possible utility of this material after reduction to metallic lead in a blast or electric arc furnace might be worthy of consideration if no more preferable forms of residues are found.

4. Lead nitrate of satisfactory quality can be made from electrotype dross. The Cu and Sb impurities in this material can be quantitatively removed by electrodeposition with metallic iron.

5. The separation scheme $Pb^{++} \rightarrow PbSO_4 \rightarrow PbCO_3 \rightarrow Pb(NO_3)_2$ with removal of all soluble impurities by filtration and washing of precipi-

tate failed to yield a product of satisfactory quality when applied to lead nitrite solution made from Essex Metal dross. Further purification by means of Y.P.S. treatment might make such a system satisfactory.

6. All residues used in lead nitrate manufacture should be freed from water soluble impurities such as Cl^-, $SO_4^=$, etc. prior to nitric acid conversion.

7. Quantities in excess of the following amounts of impurities, expressed as a % of the lead nitrate weight, have been found detrimental to quality in Y-469-D type processes.

a. 1% Ca b-1% Mg C-4.8% Zn d-.5% Ni e-.5% Cd.

b. The use of sodium ferrocyanide will not quantitatively remove Zn, or Ni from lead nitrate solutions, although in the case of the latter some beneficial effect results.

PATENT REVIEW

Nothing of a patentable nature has been developed in these studies.

EXPERIMENTAL DETAILS

The Chemical Division's participation in this matter started on 11/7/51. The original objective was the evaluation of a sample of lead nitrate liquor made by Quality Control from Bers combined flue dusts. This original objective was expanded on 11/9/51 to full scale cooperation with Quality Control in all matters related to the manufacture of lead nitrate from lead dusts or drosses under consideration, and was terminated on 12/3/51, due to a change in the lead supply situation.

The following activities have been stressed during this period:

A. Evaluation of Quality and Yield of lead nitrate ex Bers Smelting and Refining Company flue dusts.

B. Purification and evaluation of lead nitrate ex electrotype dross (Essex Metals OU 1872).

C. Determination of effects upon Quality of possible metal impurities.

1 - Examination of N-41 Solutions ex Bers Combined flue dust

A sample of lead nitrate solution (51-1672) was submitted to the Chemical Division by Quality Control for functional test in a Y-469-D type process. An examination of this material showed the presence of excess quantities of Cl^- which in fact had partially precipitated out of the cold solution as $PbCl_2$. The bulk of the $PbCl_2$ was removed by filtration and a functional test made in a Y-469-D process. All halogens used in the standard process were omitted, and the heat development cycle

was increased from 15 to 25 min. at 200°F because of the observed tendency for yellows from such N-41 liquors to convert from the rhombic to monoclinic phase at a slower rate than normal. These tests demonstrated that the lead solution used in this fashion was equivalent in quality to standard plant N-41 solutions. (See 1421-2).

Quality Control subsequently prepared N-41 solutions 51-1676, 51-1677 by preleaching Bers dry flue dusts with water, prior to nitric acid attack, to reduce the Cl^- content in the resultant N-41 solution. This was found to be unsatisfactory, because appreciable amounts of Cl^- were found in the N-41 solutions, despite the fact that the original material was washed to a very low Cl^- level. These solutions were tested in a Y-469-D process and one of them was found to give a satisfactory yellow (51-1677), the other an unsatisfactory yellow (51-1676). Spectrographic analysis of the lead nitrate solutions utilized showed the presence of minor amounts of Cd in the sample 51-1676 which in all probability accounts for the inferior performance of that sample. Samples 51-1676 and 51-1677 were prepared for extraction in different fashions i.e., 51-1676 was calcined prior to water wash and 51-1677 was not. Whether or not this is the basic reason for the different Cd contents cannot be stated from the information at hand.

Analysis of $Pb(NO_3)_2$ Solutions ex Bers Combined Dusts

Sample History	% $Pb(NO_3)_2$	gr/ml $Pb(NO_3)_2$	Total solids gr/ml	Unidentified solids	Soluble Cl^- of % $Pb(NO_3)_2$
51-1675 calcined-unleached	13.28	.166	.368	.202	3.01
51-1676 calcined -leached	27.14	.360	.463	.103	.96
51-1677 leached	24.50	.315	.407	.092	1.43

2 - Selections of Bers flue dusts

A trip to the Bers Smelting and Refining Company was made on November 10, 1951 by the writer, Mr. R. Gedd of Quality Control and Mr. E. W. Roberts, metallurgist with the Engineering Department. The purpose of this trip was to ascertain the nature of their processes with the possibility of obtaining materials with a lower content of chloride or other impurities. Mr. Robert's report summarizes our findings, and a copy of this is attached. Material supposedly lower in chloride content was available from the reverboratory furnaces and samples were obtained.

3 - Lead Yield on Nitric Acid Attack of Bers Reverboratory Sludge

An analysis of the results of experiments conducted by Quality Control indicated the possibility of very low solubility of these sludges in nitric acid. The analytical method used by the Plant Analytical

Laboratory uses a very large excess of nitric acid (134 mols HNO_3/mol Pb) to determine total soluble lead in a given sample. This is obviously far in excess of any reasonable operating excess for plant practice.

An experiment was planned to determine the effect of varying the ratio of nitric acid to lead or preleached Bers reverboratory sludge. The following table summarises the data obtained in this study.

Sample	Wt.of dry sludge* in grs.	Molar ratio HNO_3/Pb	Wt.of Sol. $Pb(NO_3)_2$ recovered in gr.	% of theoret. $Pb(NO_3)_2$	Wt.Cl^- parts 1,000,000	Wt.of Insol. Res. in grs.	ANAL.OF RESIDU HNO_3 sol. Pb %	H_2O sol. Pb %	Tota Pb %
A	405	2.5/1	81.66	20.7	58.7	327.4	15.7	.22	59.9
B	405	5/1	85.12	21.6	58.0	327	14.27	.19	60.(
C	405	7.5/1	76.86	19.5	57.0	324.4	13.52	.13	60.2
D	405	10/1	76.87	19.5	84.4	329.4	14.1	.14	59.9

* Sludge = 60.9% HNO_3 soluble Pb (dry basis)
65.34% total Pb (dry basis)

These data indicate the following:

1. Preleaching of reverboratory residue has not lowered Cl^- content to a limit considered safe for stainless steel.

2. Recovery of nitric acid soluble lead lies between 19-20% under the experimental conditions tested with a maximum of 91% of the total lead accounted for.

3. Analysis of the residue shows a small amount of water soluble lead, a considerable amount of nitric acid soluble lead, but in an amount not sufficient to account for the missing yield.

4. Possible explanations for these low conversion results under these experimental conditions are:

   (a) oxidation of $PbS \rightarrow PbSO_4$ in dilute nitric acid
   (b) lesser solubility of $PbSO_4$ in dilute HNO_3 versus higher solubility in the more strongly acid solutions used in the Plant Analytical method.

5. No functional tests have been made on these solutions.

These results indicate that Bers reverboratory sludge is not a suitable raw material for the manufacture of lead nitrate by a process analogous to the one presently in use by the plant. The possible utility of this material after reduction to metallic lead in a blast or electric furnace might be worth consideration if no more preferable forms of residues are found.

4 - Purification of Lead Nitrate from Electrotype Residues

A. Quality Control has studied lead nitrate made by attacking electrotype dross with nitric acid and found that it is readily soluble. This material contains a high percentage of impurities as can be seen from the following table:

Analysis of Essex Metals Electrotype Dross (O.U. 1872)

Cu	2.6	→	6.8%
Sn	4.7	→	5.16%
Sb	3.2	→	3.32%
Fe	.57	→	.7%
Ni	.16	→	.2%
Nitric acid soluble Pb	69	→	71.1%
Total Pb	71.8	→	75.77%
Cl^- Positive Qualitative test			

This material was found to be unsatisfactory because of the high Cu, Ni and Sb content. Attempts to purify such solutions by means of interaction with freshly precipitated PbS were made by Quality Control without complete success.

A successful separation of the Cu and Sb from the lead nitrate has been made by means of metal replacement with iron (which can be more easily removed).

$$Cu^{++} + Fe^{\circ} \rightarrow Fe^{++} + Cu^{\circ}$$

$$2\ SB^{+++} + 3\ Fe^{\circ} \rightarrow 3\ Fe^{++} + 2Sb^{\circ}$$

Such solutions, either before or after filtration of sludge remaining from nitric acid attack, can be quantitively freed of copper by iron replacement at a pH of 2.5 and temperature of 160-180°F. The reaction time will of course be dependent on surface area of iron exposed. Subsequent removal of the copper-plated iron and copper dust, followed by H_2O_2 treatemnt of the filtrate to oxidize Fe^{++} to Fe^{+++} and pH adjustment to 3.5, was found to precipitate iron to the usual extent reached in N-41 plant practice. Clarification of the solution gave no appreciable difficulty.

Cost of H_2O_2 Treatment

Assume Cu = 4 pts/70 pts Pb

$$\therefore \text{Basis } 207\#\ Pb = \frac{4 \times 207}{70} = 11.82\ \#\ Cu$$

$$\underset{63.54}{Cu^{++}} + \underset{56}{Fe} \rightarrow Cu^{\circ} + Fe^{++}$$

$$\therefore \text{lbs. } Fe^{++} \text{ to be oxidized by } H_2O_2 = \frac{11.82 \times 56}{63.5} = 10.3\#$$

$$2\ Fe(NO_3)_2 + H_2O_2 + 2HNO_3 \rightarrow 2\ Fe(NO_3)_3 + 2H_2O$$

$$2\frac{10.3}{x\ 56} \times 34 = 3.14\ \#\ H_2O_2 \text{ at } \pm .75¢ \text{ lb.} = \$2.35 \text{ per } 207\ \#Pb \text{ or } 331\ \#Pb(NO_3)_2$$

Solutions made in this fashion were found to be satisfactory by standard Cu, Fe and Sb tests, but contained Cl^- and Ni^{++}. An attempt to remove the latter by means of a Y.P.S. treatment was not fully successful, (due apparently to the much lower solubility of lead ferrocyanide). However, the yellow produced by the Y.P.S. treated N-41 was better than untreated N-41 in lightfastness.

N-41 made in this fashion compared satisfactorily against standard N-41 plant solutions in a Y-469-D procedure, despite the presence of Cl^- and Ni^{++}.

B. A further attempt to purify this liquor by means of the sequence:

(1) $Pb^{++} + Cu^{++}, Fe^{+++}, Sb^{+++}, Cl^- + SO_4^{=} \rightarrow PbSO_4 +$ soluble impurities to be removed by filtration and washing

(2) $PbSO_4 + Na_2CO_3 \rightarrow Pb\ CO_3 + Na_2\ SO_4$ filter off $PbCO_3$- wash out $SO_4^{=}$

(3) $PbCO_3 + 2HNO_3 \rightarrow Pb(NO_3)_2 + CO_2 + H_2O$

was unsuccessful. The final N-41 solution contained excessive amounts of Cu^{++}, Fe^{+++}, and Cl^- but was free of Ni^{++} and Sb^{+++}. This material was unsatisfactory in a functional test as Y-469-D. The impurities present must have been adsorbed during precipitation of the $PbSO_4$ and $Pb\ CO_3$, and could not be completely removed by washing.

5 - Effect of Impurities in N-41 Solutions

Functional tests have shown that amounts of metals in excess of the quantities suggested below are definitely harmful to Y-469-D type processes (expressed as % of $Pb(NO_3)_2$).

.5% Cd (found in N-41 ex Bers Dross 51-1676)

4.8% Zn, .5% Ni, 1% Ca, 1% Mg

Attempts to remove Zn^{++} from N-41 solutions with sodium ferrocyanide have been shown to be unsuccessful, presumably because of the greater insolubility of $Pb_2Fe(CN)_6$ under the conditions tested. Amounts of Y.P.S. equal to twice that required by the zinc present were insufficient to remove all of the zinc.

Typical Analysis Bers Combined Lead Dusts

	Wet Separation Dry Basis	Dry Separation Dry Basis
Total Pb	70.18	58.82
HNO_3 sol	69.96	56.04
Sb	3.10	3.71
Sn	.06	.04
Bi	.04	.084
Fe	2.23	5.62
Cu	.012	.55
Ni	0.011	.008
As	.051	.09
S	?	?
Zn	.03	.012
H_2O	19.87	.10

Qualitative Tests Ca^{++}, Mg^{++}, Cl^-, $S^=$, $SO_4^=$ $SO_3^=$ organic matter present

REFERENCES

1. DSN 51-33
2. NB 1421-1-9
3. Monthly Summary Inorg. Lab. November - December 1951

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