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Chicago — Auxiliaries Research

Cleveland — Auxiliaries — July 31, 1956

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New Jersey Zinc Company
- Report on visit to their Lithopone Plant at Depue, Ill. -

At your request and as per arrangements made by you, Mr. Leeds, Mr. Wyman and the writer visited the lithopone plant of the New Jersey Zinc Company at Depue, Illinois on July 26, 1956.

The purpose of this visit was to inspect the equipment in the plant for possible use by Sherwin-Williams Company, to study their process and to learn how New Jersey makes their various grades of lithopone. This visit was made possible by the fact that New Jersey Zinc Company is discontinuing the manufacture of lithopone. (Based on information obtained at Depue, New Jersey plans to continue the manufacture of zinc sulfide at their Palmerton plant. As a matter of fact, they now plan to run the zinc sulfide plant continuously at reduced production instead of at full production intermittently. This new practice is to reduce the amount of off-grade zinc sulfide caused by intermittent operation.)

We were shown through the lithopone plant by Mr. Neil Banks, General Superintendent of the Depue plant and by Mr. C. W. Geppelt, Manager of the lithopone plant. After inspecting the lithopone plant, Mr. Banks took us on a tour of the Zinc Smelter Plant where we saw the making of brickets (formed by compressing soft coking coal and zinc ore), coking of the brickets, charging of the vertical zinc retorts, discharge of the molten zinc metal and casting of zinc metal. We also saw the cadmium-zinc-lead stills used to separate cadmium, zinc and lead. Some of these were in the process of being rebuilt due to damage caused by the recent strike.

The lithopone plant includes also a zinc sulfate plant and a black ash plant as an integral part of the lithopone manufacture. No zinc sulfate or barium sulfide is made for other purposes.

BLACK ASH DEPARTMENT

Sheet C lists the equipment used and the details of flow.

There are two Rotary Kilns, but only one is now in operation. The kilns are 53 feet long, 6 feet inside diameter. The kiln rotates about 50 seconds per revolution (53 sec./rev. by actual count). The kiln is lined with Superior brick made at Depue. They use, with considerable success, Luminite to head the kilns. This may be made into a thick or thin slurry and molded for the purpose. The header brick are held in place by bolts with square heads, counter sunk into the brick.

These bolts connect the brick to a flange. Little trouble is experienced from burning the heads off the bolts. There is no seal between the tube and head. The head is left partly open. There is a hole about 1 ft. square at top section and a smaller hole at bottom section for viewing the burning.

The back end of the kiln is fairly well sealed (but not as well as they would like). The temperature of the charge is about 1200-1400 near the discharge end and about 800-900°C. in the back or feed end of the kiln. Because of the extreme heat at the back end, they have more trouble from refractory at the feed end. Furthermore, it is necessary to keep two good streams of water impinging on top of the back end of the kiln to reduce the temperature and burn-outs. In order to reduce dust loss, which is still somewhat high, the gases are discharged into a large refractory tunnel fitted with baffles to increase travel and fall-out. This tunnel is connected to the stack by a breach. The breach and stack are fully lined. Stack is about 4 feet outside diameter.

The charge to the kiln is usually

180-200# dried petroleum coke
850# Barytes

giving about 21% carbon in the roast. The barytes usually used is 94% beneficiated ore.

The black ash, discharging into hopper cars, usually has about the following composition:

87-88%	BaS
1 1/2% or lower	$BaCO_3$
3-4% (?)	BaO

Iron is considered undesirable because it removes S, increasing the Ba loss. The kiln is operated on the oxygen side, usually about 1/2% oxygen. This prevents "ringing".

Mr. Jeppelt did not believe that 97-100% ore was any better on recoveries than 97% ore.

About 37-38 tons of black ash are produced per day per kiln.

The black ash is leached in a 5-tank countercurrent system. Instead of filtering, the solid discharge from the countercurrent system is passed to settling tanks. Mr. Jeppelt believes that a filter would be preferable.

The BaS liquor is stored in lined wooden tanks equipped with internal heaters.

The BaS liquor has about the following properties:

12-14° Be at 70°C.
1120 Sp. Gr.
About 120 g./l. of BaS
Chloride - 0.02 g./l.
SH - 47.2%, Range 46-48

(No effort is made to control SH of liquor. Gravity is not considered too important from a quality standpoint.)

<u>ZINC SULFATE DEPARTMENT</u>

Sheet 8 lists the equipment and details of flow.

The zinc material for leaching is usually zinc oxide (Largely scrap). Roasted Hanover ores and Cannister dust may be also used.

The leaching tanks are lead-lined wooden tanks with no agitation.

The H_2SO_4 and oxide are added to the leach tanks and allowed to seep to permit solution and also to let the undissolved portion to settle to a clear solution. The clear liquor is then pumped off and the solids releached, washed by decantation, and finally filtered. The releached liquor and filtrate are returned to leach tank as dilute liquor.

The liquor from the leach tank is pumped to the aeration tanks where most of the iron is removed by abundant aeration through 4 large pipes (4") equally spaced around the tank. Lime (or $CaCO_3$) or zinc oxide may be added to aid in removal of iron. Occasionally, $CuSO_4$ is added to reduce nickel. Zinc dust is added to remove excess copper. The Baume of the zinc liquor is not considered too important, but is usually kept at about 30° Be at 65°C. The nickel content is kept below 0.0001% in the liquor. They would prefer as low as 0.00002%.

After settling, the clear liquor is pumped to manganese tanks. $KMnO_4$ is added to remove Mn and last traces of iron. This liquor is filtered into cadmium tanks where Cd is removed by zinc slabs.

This is filtered and sent to the Zn Storage Tanks. The residue is treated for Cd recovery.

Brass pumps and lead-lined pipes are used in the $ZnSO_4$ plant.

The overall recovery of zinc in the plant is 91%. 90% recovery is made when leaching ore and 95% on refuse oxide.

The zinc sulfate liquor has about the following properties:

1240-1250 Sp. Gr. at 65°C.
Approx. 30° Be at 65°C.

LITHOPONE MANUFACTURE

Sheet "A" gives the layout of the Lithopone Plant. Sheet "D" gives the flow sheet for the manufacture of lithopone proper.

As a whole, the Depue lithopone plant is somewhat antiquated and has purposely not been kept in good repair due to less emphasis on lithopone. The process reminds one of the old Chicago lithopone plant, but only in part, as the latter was more modern in many respects than the former. Both plants operated more on a batch proposition than the Coffeyville plant, making it possible to change easily and quickly from one grade to another, both regular and special, but required more hand labor.

Both plants make free use of labor-consuming plate presses (Shriver) and also both made use of tunnel dryers for both crude and finish lithopone. In the Depue Plant, the press cake is dropped from the filter press into a car. It is then shoveled by hand onto the pans for drying; whereas, in the Chicago plant, as I recall, the press cake was dropped directly onto the drying pans, which were then placed onto the rack to be sent to the tunnel dryer.

The Depue plant uses the vertical tube muffles instead of rotary kilns as used at Chicago and Coffeyville. These muffles are in tandem with five pairs to a battery. There are five batteries, each discharging into a separate open quench box. The crude to the calciners is kept slightly moist. It must not be dry, but the moisture content is not determined except by observation and feel.

Calcination is accomplished by hot gases conducted through a jacket around the tube containing the lithopone. A gas-fired furnace produces the hot gases which are pushed through the space between the jacket and the calciner tubes. These hot gases are not recycled, but allowed to escape into the stacks after one pass.

The calciner tubes are 38 feet long (with about 37 feet in the hot zone) and 7 inches inside diameter with a wall-thickness of about 1/2 inch. The tubes are composed of two lengths welded together. The lower 3/5 or 2/3, which is in the hottest zone, are galvanized. Experience has shown that galvanized iron resists the heat of the hot gases better than the plain iron. The life of these tubes is about 18 months.

These vertical tube muffles permit lower calcining temperatures for long periods of time with less sintering than the internally-fired kilns like the ones at Coffeyville. They have the serious disadvantage of over-calcination next to the tube and under-calcination in the center of the charge. Furthermore, as the tubes become corroded, heat transfer is reduced. The tubes, fed from the top, are pounded every 15 minutes to keep the charge moving downward. This continual jarring of the tubes causes scale to fall off and contaminate the lithopone with iron. The iron is removed by powerful electromagnets placed at strategic points along the flow of the dried finish lithopone as it travels to the pulverizers.

Each battery (10 tubes) will produce about 15 tons per day, making the capacity of the five batteries about 75 tons of lithopone per day.

Mr. Geppelt said that he did not believe it was possible to operate these tube calciners on the discharge from mechanical (continuous) filters since they do not produce a sufficiently hard or firm cake like the Shriver press cake.

Mr. Geppelt said that he preferred the externally fired, rotary calciners to the vertical muffles. The Palmerton lithopone plant was equipped with this type of muffles. Mr. Banks showed us one of these muffles which is now being used to concentrate cadmium. These calciners are very much like a short version of the calciners at Coffeyville with a furnace built around them. They are, of course, unlined and are made of heat resisting alloy. They are supported on trunions on the ends extending out of the furnace wall. (Dupont used also an externally fired calciner but shaped like a pipette with the bearing on the restricted ends. The bowl had a smaller diameter than those used at Palmerton. The DuPont muffles were about 2 feet in diameter; the Palmerton about 4 feet in diameter.)

Indirect firing of these calciners permit more freedom in preparation of the crude than is possible in an internally fired calciner. Indirect firing has the distinct advantage of producing a softer quench.

The quench from the muffles is pumped to Abbe Pebble Mills. These are batch operated requiring about 5-6 hours pebble milling to obtain the desired degree of fineness. (These cylinderical pebble mills are about 12 feet long.) Mr. Geppelt prefers Belgium Silex blocks and Danish pebbles.

One of the Abbe pebble mills has been altered to permit continuous operation. A portion of the production flows through this; the rest through the batch operated mills.

The discharge from the Abbe mills may be further reduced in fineness, as determined on a 325-mesh screen analysis, by passing through a Charlotte Colloid Mill. Some grades by-pass the Charlotte mills; others are given one pass; the fine-textured grades are given two passes. The plant is equipped with six Charlotte mills.

No classifiers are used in the Depue plant. Mr. Geppelt feels that centrifuges (Bird) are desirable, and would increase the efficiency of their wet grinding system. The Palmerton plant used Bird centrifuges.

The finish pulp from the milling system is filtered in Sweetland Presses. These open from the bottom permitting the cake to drop onto a vat car from which it is shoveled onto trays for drying in the Tunnel Dryers.

The dried, finish cake is broken up to a fairly uniform size and transferred to the dry milling system by elevators and belt conveyors.

Iron particles or bolts are removed on the belt conveyors by powerful electromagnets as previously stated. Dry treatments are also made on this belt.

The elevators lift the lithopone to bins from which it is fed into the Stedman Disintegrators.

Like DuPont, New Jersey emphasizes the importance of producing a soft quench, use of good wet milling and no "dry milling", only disintegration. DuPont used Mikro Pulverizers; Depue used a No. 40-B Stedman Mill.

Packing is done in porous bags to permit the escape of air from the bags when compressed in the hydrolic press. This compression is done on heavy cardboard with one side creased to fold about 4 inches from the edge to permit the fork to be inserted under the load in the warehouse or car. They experience little or no slippage of the bags in transit. (Treated bags to prevent slippage are too tight to permit the escape of the air during compression.) Unless the air escapes, the bags explode.

The following sheets and diagrams are attached to copies of this report for Mr. Coolidge, Mr. Deeds, Mr. Jones, Mr. Ashmer, and the writer:

1. Lithopone Department Lay-Out Sheet A.
2. Zinc Department Flow Sheet B.
3. Barium Department Flow Sheet C.
4. Lithopone Department Flow Sheet D.
5. Lithopone Precipitation Sulfur Addition Table.
6. Blueprint of Continuous Precipitation Tank (Simultaneous Strike)
7. Tank Capacity and Bin Storage

Striking

Because of the close relationship between striking methods used at Depue and the various Albalith Grades of lithopone, precipitation has been purposely placed out of logical order, so as to discuss as an introduction to the "bases" used for the different grades.

Two methods of striking are used at Depue. These are identified as:

1. Process "A". This is a zinc first strike made in a tank equipped with a gate agitator with the legs only in the liquor. The agitator rotates about 14 seconds per revolution.

   About 16" of 30° Be zinc sulfate liquor is placed in the tank. Chloride is adjusted for the grade desired. The BaS liquor (12-14° Be) is then added with agitation to the desired endpoint as determined by OH titration.

Run pH and add the amount of sulfur as indicated by practice for the period and the Sulfur Table for the desired grade.

The required striking time for a 5-ton batch is about 1 hour and 10 minutes.

Pump to crude storage tank for settling.

2. Process "C". This is a simultaneous strike made in the Continuous Precipitation Tank, leading with zinc at a pH of about 5, brown (close to black) with Congo Red.

The BaS liquor is added in the well near the center of the tank. This well also contains the Lightning Mixer agitator turning about 460 RPM. The $ZnSO_4$ liquor is added about 6" from the perifery of the tank. See diagram for details.

The particle size may be varied by changing the position of the outlets and by changing the level of the liquid in the tank.

The overflow from the precipitator flows to a tank for final adjustment for the desired grade.

<u>Endpointing</u>

<u>OH</u> - Titrate 250 mls of the filtrate from the strike tank or adjustment tank with 0.25N HCl to the endpoint for phenolphthalein. The OH value depends on the base desired. (The endpoint is fugitive).

<u>SH</u> - Add 2 or 3 drops of HCl to restore endpoint to the filtrate used to determine OH. Pipette off 25 mls and titrate with 0.1N I_2 solution to a starch endpoint. This is called the SH. The SH value depends on the base desired and also indicates, when used with the Sulfur Table, the amount of sulfur to add.

<u>Bases</u>

There are four bases used to make Albalith Lithopones. These are:

1. Blue Label
2. Black Label
3. Red Label
4. Green Label

Each base is used to make a variety of grades of lithopone. Each grade may be processed or treated quite differently even though made from the same base.

The bases and corresponding grades are described in detail on the following pages.

I. BLUE LABEL (BASE)

1. Grades - Albalith 10, 90, 332, 362.

2. Process "A" - Zinc First Strike.

Albalith 362 (332) may also be run by Process "C". This will give a softer quench. Palmerton used Process "C" for Albalith 362 (332).

3. Chlorides

a. Preferred - 0.05 g./l. in $ZnSO_4$ liquor at 20° Be at 20°C.

b. Range - 0.01-0.08 g./l.

c. For Albalith 90, keep chloride at 0.05 g./l.

4. OH (Crude Filter Press Liquor)

Range - 1.8-2.0 (Except for Albalith 362 (332). See Special "Adjustments" for these grades.

5. SH

Use Column 1 x of Sulfur Table for Albalith 10 and 90. Make no adjustment in SH for Albalith 362, which is the base for Albalith 332.

6. Adjustments - To make Albalith 362 (332), make the following special treatments:

a. End-point strike to neutral to Congo Red or phenolphthalein.

b. Add 30#/ton of lithopone of aluminum sulfate, $Al_2(SO_4)_3 \cdot 12H_2O$ to finished strike. (Aluminum sulfate is supplied by DuPont at low Fe content, specially selected for them at not over 0.005% Fe).

c. Bring pH back with BaS to phenolphthalein.

d. Add 10#/ton of Na_2SiO_3, S grade.

e. Then add about 10#/ton of H_3PO_4 to bring the SH to 0.9-1.1.

f. Bring OH to 1.2-1.4 by adding $Ba(OH)_2$. This requires about 45#/ton lithopone.

7. Calcination - About 875°C. for about 6 hours. See Tinting Strength for control.

8. Equalizer

9. <u>Pebble Mill</u> - Mill for 5-6 hours to a fineness of 0.35-0.5% on 325 mesh screen.

10. <u>Charlotte Colloid Mill</u> -

a. Regular to 0.35% on 325 (Single Pass).

b. Albalith 90 to 0.01-0.02% or as low as 0.005% on 325 (Double Pass).

c. Albalith 362 (332) is not passed through the Charlotte Mill.

11. <u>Treatment (Dry)</u> - To make Albalith 332, add 1/2% of $Na_4P_2O_7$ to Albalith 362 material on conveyor belt to Stedman Mill.

12. <u>Stedman</u>

a. Regular - Single Pass.

b. Special - Give double pass to Albalith 90.

13. <u>Tinting Strength</u>

a. Calcine regular grades to a tinting strength of 100.

b. Calcine Albalith 90 to a tinting strength of 97.

c. Calcine Albalith 362 (332) to a tinting strength of 88.

II. BLACK LABEL (BASE)

1. Grades - Albalith 11, 73, 807.

2. Process "C" - Simultaneous Strike.

3. Chlorides

   a. Preferred - 0.10-0.20 g./l.

   b. Range - 0.10 to 0.25 g./l.

4. pH (Crude Filter Press Liquor)

   Range - 1.8-2.0

5. SH - Use "3 x" column in Sulfur Table for Albalith 11, 73, 807.

6. Calcination - 850°F. for 6 hours or T.S. 100.

7. Equalizer

8. Pebble Mill - 5-6 hours to 0.35 to 0.5% on 325 mesh.

9. Charlotte Colloid Mill

   a. Regular - Single Pass

   b. Special - Albalith 807, Double Pass

10. Treatment (Dry)

    For Albalith 73, treat with 0.7% AAS Lauric Acid (Drew Co.) by spraying the molten acid onto the dry material before dry milling.

11. Stedman - Single Pass

12. Tinting Strength - 100. (Calcine to keep T.S. at 100 Min.)

III. RED LABEL (BASE)

1. Grades - Albalith 13, 14, 806, 14A, 14B.

2. Process "C" - Simultaneous Strike.

3. Chlorides

   a. Range - 0.65-0.75 g./l.

   b. Special - Keep Albalith 13 at 0.65 g./l. (Green Label at 0.65 g./l.)

4. pH (Crude Filter Press Liquor)

   a. Preferred - 2.6-2.8.

   b. Range - May be as high as 4.0.

5. SH - Use "3 x" column of Sulfur Table for Albalith 13, 14, 806, 14A and 14B.

6. Calcination - 825°C. for 6 hours. Vary temperature to get T.S. of 100.

7. Equalizer - For Albalith 14A and B only, the soluble salt content is reduced to a specific resistance of 20,000 ohms. This is done as follows:

   Dilute with water to 50% of volume and add H_2SO_4 to a fair yellow endpoint to bromothymol blue. Let settle and decant. Wash 3 times as above by dilution and decantation.

   For Albalith 14B, the zinc oxide is reduced to 0.01%. About 5# of sulfur per ton of lithopone is added to help reduce zinc oxide.

8. Pebble Mill - 5-6 hours to 0.35-0.5% on 325 mesh.

9. Charlotte Colloid Mill

   a. Regular - Double pass to 0.05 max. on 325.

   b. Special - Albalith 13, None.

10. Treatment (Dry) - None

11. Stedman - Single Pass

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12. Tinting Strength - 100. Calcination temperature is purposely kept low to reduce cost. The temperature is usually kept just high enough to get a tinting strength of 100. Higher temperatures would increase the tinting strength to 105 or higher on these grades.

IV. GREEN LABEL

Special for Columbus Coated.

Same processing as Red Label, but keep Cl at 0.65 g./l.

At the present time, production is divided about as follows:

40% Blue Label
40% Black Label
30% Red Label

The Blue Label includes Albalith 362 (332), 90 and 10. Mr. Jeppelt estimated that roughly the production on Blue Label was divided about as follows:

50% Albalith 362 (332)
40% Albalith 90
10% Albalith 10

This breakdown does not agree with some previous figures and are probably not too accurate as Mr. Jeppelt was just giving a rough guess. He did, however, emphasize that Albalith 90 represented one of the large volume grades along with Albalith 362 and Albalith 73.

At the present time, plant production of all grades amounts to about 1250-1400 tons per month. This is equivalent to about 15,000-16,800 tons per year.

The data in regard to the liquors and grades of lithopone has been rechecked with Mr. Jeppelt and should be accurate. In most cases, he consulted the records to check the data, and in other occasions, he did go by memory.

In regard to the plant equipment, I think we should review the suitability of the Lehigh Mills for pulverizing silica. If these mills are suitable for this purpose, it might be well, should we decide to investigate thoroughly the silica deposit in Northern Arkansas, to consider purchasing one or both of these mills.

The two Black Ash Kilns would be suitable for any operation involving the need for kilns of this size, but may be too large for most of the anticipated use of kilns based on the present developmental program.

I believe it might be well for us to consider purchasing one or two of the Abbe mills if these can be obtained at a reasonable price, as they can be made into continuous pebble mills, as they have already done at Depue with one of them. I feel that in spite of the fact that we have rake classification in our wet milling system in Coffeyville, that our wet milling is still considerably inadequate for the production of fine textured lithopone. A Bird centrifuge will, of course, increase the efficiency of milling and is highly desirable. I think we must face the fact that our internally fired calciners do sinter the particles and make them difficult to grind, so that it is important for us to do a thorough job of wet milling. If we are to try to match such lithopones as Albalith 90, we should give serious consideration to improving our wet milling system. As an aid in this work, I would suggest also that we consider obtaining two or three of the Charlotte Colloid Mills to further improve the fineness of our material before drying.

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If these mills are in good shape, they should improve the texture of our lithopone as New Jersey, to obtain the finest textured materials, make two passes through the Charlotte Mills.

I think we must recognize that our calciners and dryers are not conducive to the best textured materials. For this reason, we have to resort to extra precautions in dry milling by the use of most efficient Raymond Mill set-ups. I believe, however, that if we could do a better job of wet milling, that we could cut down on the dry milling, particularly if we can overcome the objection to the rotary dryers. I think we all agree that for most purposes, Mikro-Pulverizers and Stedman mills give a more desirable type of lithopone if the base material is in the proper condition.

We cannot, of course, produce the same type of quench as they get with their externally-fired tubes in our internally-fired calciners, but I think we can improve the situation.

I would suggest also that we give serious consideration of obtaining the Stedman Mill if this is available in reasonably good condition and at an attractive price. It seems that we always have the need for such mills, as we no sooner remove a mill from one part of the plant than we find a need for it in another. This might be an appropriate time to obtain a Stedman Mill.

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CED.
JAS.
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