

CALUMET AND HECLA CONSOLIDATED COPPER COMPANY
CALUMET, MICHIGAN

January 7, 1946

Mr. W. J. Harshaw, President
The Harshaw Chemical Company
1945 East 97th Street
Cleveland, Ohio

Dear Mr. Harshaw:

I thought you would be interested at this time in a brief report regarding the progress of the construction work for the Lake Chemical Company.

Construction at Tamarack seems to be progressing satisfactorily and there is every indication at this date that there will be no delay in installing equipment as received. The lower floor is completed and all foundations for supporting the reaction tanks and the reaction floor are ready to receive steel columns. Fabrication of steel is under way in our shops and all material for the floor is either on hand or en route.

Construction schedule calls for completion of this floor by mid-February, at which time installation of reaction tanks may be started. These tanks are being constructed in the Calumet shops. Shipment and installation of temporary tray dryers from Harshaw can be scheduled for the same date.

Delivery of equipment from manufacturers is delayed and most of the original promises have been revised backwards. Electrical equipment, especially 25 cycle motors, is particularly slow moving, but we are hopeful that we can substitute temporary, though possibly inefficient sized units, for the very late deliveries.

Physical transfer of equipment used for the development and manufacture of copper hydrate will be made as foundations become available for permanent location of these units. Accurate record was kept by Calumet of the cost, and financial transfer to the account of Lake Chemical Company can be made at an appropriate time, after approval by The Harshaw Chemical Company.

Yours very truly,

President

ERL:hgm

Mr. A. H. Wohlrab.....2.....1/29/46.

more efficient handling; there would need to be some other consideration to make it profitable. The fact that we could design a much more compact leaching building, lower than the present type, and that we could install square leaching tanks instead of round ones to use space more effectively would save considerable money both in heat and in handling. The still house, of course, would be part of the same building.

January 29, 1946

Mr. A. H. Wohlrab, General Manager
Calumet & Hecla Cons. Copper Co.
Calumet, Michigan

Dear Sir: We have learned enough about handling secondary copper in winter to know that we do not care to go through another under the same conditions we have been up against during this one.

The plans are for a new broad gauge track in the east end of the electrolytic plant by means of which cars can be brought in from the south and unloaded and baled under the cranes. We cannot, however, use the whole electrolytic plant for storing secondary even if we baled it all, as we expect to do now with the two baling presses.

We should have a building for handling secondary and it ought really to be attached to some other plant so that handling will not have to be done twice. For this winter we have not planned on doing any stripping to speak of but that cannot go on indefinitely. All of our operations will have to be carried on in winter as well as in summer. Under the present conditions we cannot keep shipments separated sufficiently well nor can we always find material when we want it. We have a plan of the yard showing the locations of all piles but even so we cannot always reclaim them especially when the work has to go on during snow storms.

To avoid rehandling it is advisable to store secondary copper in pans or in some other suitable receptacle - that is, a container convenient for charging. We will need many more than we now have.

You know that for some time I have been obsessed with the idea that we should have our leaching plant adjacent to the smelter so that all handling whether of material smelted or of material leached could be done by the same crew. The present method is decidedly wasteful. We could not, however, hope to pay for a new leaching plant on the basis of savings made by

Mr. A. H. Wohlrab.....2.....1/29/46.

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Mr. A. While discussing this matter with Mr. Jones it occurred to us that perhaps we were overlooking a bet in not investigating the belt conveyor system of leaching more thoroughly. Neither Bob Poull nor myself would have time enough at our disposal to do experimental work of that kind but it would take a man who could design and install equipment and also supervise the operation. I approached George Craig to see if Lawrence Klein might have any free time on his hands but evidently he will be needed for the chemical plants at Tamarack. There is no other person in our organization capable of handling that sort of work. If a belt conveyor proved effective it might in itself justify the erection of a new plant. A electrolytic plant by means of which ore can be brought in from the south and unloaded and baled under the orages. We cannot, however, use the two baling presses for storing secondary even if we baled it all, as we expect to do now with the two baling presses.

Yours very truly,
HCK

We should have a building for baling secondary and it ought really to be attached to some other building so that handling will not have to be done twice. For this winter we have not planned on doing any stripping to speak of but that cannot go on indefinitely. All of our operations will have to be carried on in the open. Mr. E. R. Lovell is in charge. Under the present conditions we can separate secondary separately well nor can we always find material when we need it. We have a plan of the yard showing the locations of all piles but even so we cannot always reclaim them especially when the work has to go on during snow storms.

To avoid rehandling it is advisable to store secondary copper in pens or in some other suitable receptacle - that is, a container convenient for charging. We will need many more than we now have.

You know that for some time I have been obsessed with the idea that we should have our leaching plant adjacent to the smelter so that all handling whether of material rejected or of material leached could be done by the same crew. The present method is decidedly wasteful. We could not, however, hope to pay for a new leaching plant on the basis of savings made by

February 7, 1946

Mr. A. H. Wohlrab, General Manager
Calumet & Hecla Cons. Copper Co.
Calumet, Michigan

Dear Sir:

Tamarack has now started to dry copper oxide. Within the next ten days the dried oxide will be packed in 100-lb. bags and stored at the Tamarack plant. Since the Tamarack stock will no longer be a part of the smelter inventory Mr. Jones, in order to get the dried oxide into secondary production, will carry an inventory of dry material at Tamarack as a part of the secondary copper accounts. Mr. Oxnam will pick the material up for his monthly records from Mr. Jones' reports.

Shipments of oxide in bags will be made from the Tamarack plant and the data will be reported to the smelter by Tamarack. The smelter will do the billing as before and will also take orders for dry material from the New York office.

If there is any reason for changing the above schedule will you please advise me as soon as possible?

Yours very truly,

H.C.K.

H. C. Kenny
Superintendent

HCK/C

cc: Mr. E. R. Lovell ✓
Mr. W. W. Lynch
Mr. J. G. Bennetts
Mr. W. A. Oxnam
Mr. W. F. Jones
Mr. R. K. Poull

*See letter EARL - A ON
2/8/46.*

CALUMET AND HECLA CONSOLIDATED COPPER COMPANY
CALUMET, MICHIGAN

July 5, 1946

Mr. W. J. Harshaw, President
The Harshaw Chemical Company
1945 East 97th Street
Cleveland 6, Ohio

Dear Mr. Harshaw:

Following is a condensed report covering progress being made at the Lake Chemical Company:

COCs:

The only missing equipment as of this date is in connection with the Oliver filter and we have promise of full shipment by express from Oakland, California, on July 5 so we are justified in anticipating delivery by July 12, and we have asked that John Porvasnik be here by that date to make final adjustments and get the plant into production. The raw materials, salt, sulphuric acid, ammonia and copper are here and in ample quantity. We are hoping that Porvasnik will find all the equipment and piping in good order and that he will have no difficulty in making the necessary adjustments and breaking in the operating crews.

COPPER HYDRATE:

Production for the month was 21,000 lbs., which exhausted the supply of caustic soda. Operations were necessarily inefficient and the plant should still be considered as being in the development stage. The Raymond dryer is not as yet in commission and the tray dryers were used to good advantage, but unpleasant and moderately heavy dust losses ensued when the dry product was pulverized and packaged. The bagging machine is now operating satisfactorily and the Raymond dryer and cage-mill will go into commission on the next batch of hydrate so that dust losses will be normal for the complete equipment as at present installed. There is no provision for catching the dust leaving the cyclones.

Yours very truly,

President

ERL/P

CALUMET AND HECLA CONSOLIDATED COPPER COMPANY
CALUMET, MICHIGAN

August 5, 1946

Mr. W. J. Harshaw, President
The Harshaw Chemical Company
1945 East 97th Street
Cleveland 6, Ohio

Dear Mr. Harshaw:

Following is a report covering progress being made at the Lake Chemical Company.

COCs: Production of COCS began on July 15 as scheduled. There were no mechanical defects nor difficulties encountered, and operations were remarkably smooth, with the new operators hitting their stride rapidly under the able tutelage of John Porvasnik of Harshaw. A copy of Mr. Porvasnik's report on operations to date is attached hereto.

You will note that for the time the anticipated monthly production is not in excess of 60 tons, the current bottleneck being the capacity of the tray dryers, a temporary installation. The six reaction tanks and two slurry tanks are far in excess of the anticipated final output of 150 tons monthly, but the Oliver filter product is barely up to present dryer capacity. John Porvasnik is worrying more about this than his report indicates and it is, of course, too early to evaluate possibilities of improvement in procedure, but 100% increase in output is not going to be easy to get with present filter equipment.

Copper Hydrate: Operations were limited by inability to obtain caustic soda, but an ample supply is promised for a good run beginning about August 10. The Raymond dryer is scheduled to go into operation at that time and the present pilot plant units can be given a good try-out for capacity on a continuous run. We are considering using the north (spare) COCS slurry tank as a hydrate slurry tank, which will permit continuous runs on the hydrate filter, dryer and bagging units, independent of the production rate of the reaction tanks.

We have had no adverse reaction from any of the customers as to quality of product and are getting some repeat orders. We have not as yet shipped to the Nuodex Company.

Yours very truly,

President

ERL/P
Enc.

THE HARSHAW CHEMICAL COMPANY

Mr. G. L. Craig
COPY

Mr. E. R. Lovell

OCT 16 1946

October 14, 1946.

October 14, 1946.

Mr. G. L. Craig, Director of Research,
Calumet and Hecla Consolidated Copper Company,
Calumet, Michigan.

Dear Mr. Craig:
I should talk over the Phelps Dodge activities and get fully posted on the present Navy requirements for cuprous oxide or cuprous oxide substitutes. We also can talk over cupric oxide manufacture as well.

I am sorry that my description of the proposed cuprous oxide process has not been clear so I will try to make it again in more detail.

We have started with the dried mixed oxide as furnished by you. This material is agglomerated and we have found it necessary to first ball mill it. Naturally at Calumet we would start with the mixed oxide before drying. Whether it would have to be ball milled or not will have to be determined but in either case it is not a very serious step.

This material is then leached with dilute sulphuric acid. Enough sulphuric is added to only react with the cupric oxide present in the mixed oxide. It will react with this cupric oxide preferentially to the cuprous oxide. It is here that we get some copper sulphate solution. The sulphuric acid leach is in my mind better than the acetic acid leach as we should be able to dispose of the copper sulphate liquors in our COCS operations. If an excess of copper sulphate solution is produced above what can be used in COCS there are two or three methods of disposing of same which we can discuss when you are here.

After leaching with sulphuric the copper sulphate must be removed and the material be watered. It is then furnace and a small amount of acetic acid is mixed in before feeding to the furnace. The acetic so introduced is lost but it does have a very beneficial effect on the quality of the oxide.

There is not a very big demand for copper acetate and it would seem to me that this product if we decide to make it could best be made from either your regular mixed oxide or a fairly highly oxidized mixed oxide. I do think it would be advisable, however, to keep the consideration of this separate from the manufacture of cuprous oxide because it is almost sure that the amount of copper acetate we can sell will not be in balance with the amount of cuprous oxide we can sell.

Inasmuch as you are planning to be here early in November we can discuss the whole subject very thoroughly and I think we can clarify the description of the process, and I believe you will find our reasoning is quite sound.

THE HARSHAW CHEMICAL COMPANY

Mr. G. L. Craig.

October 14, 1946.

COPY

Mr. E. R. Lovell

October 14, 1946.

Mr. G. L. Craig, Director of Research,
Calumet and Hecla Consolidated Copper Company,
Calumet, Michigan

We should talk over the Phelps Dodge activities and get fully posted on the present Navy requirements for cuprous oxide or cuprous oxide substitutes. We also can talk over cupric oxide manufacture as well.

I am sorry that my description of the proposed cuprous oxide process has not been clear and I will try to explain in more detail. I am writing our office in Los Angeles to get as much information as possible on the Alloys Company and get samples of their product. We have started with the dried mixed oxide as furnished by you. This material is agglomerated and we have found it necessary to first ball mill it. With kind regards,

Whether it would have to be ball milled or not will have to be determined but in either case it is a very serious step.

Very truly yours,

This material is then leached with dilute sulphuric acid. Enough sulphuric is added to only react with the cupric oxide present in the mixed oxide. It will react with this cupric oxide preferentially to the cuprous oxide. It is here that we get some copper sulphate solution. The sulphuric acid leach is in my mind better than W. J. HARSHAW leach as we should be able to dispose of the copper sulphate liquors in our COGS operations. If an excess of copper sulphate solution is produced above what can be used here are two or three methods of disposing of same which we can WJH:MFS
cc/Mr. E. R. Lovell here.

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Inasmuch as you are planning to be here early in November we can discuss the whole subject very thoroughly and I think we can clarify the description of the process, and I believe you will find our reasoning is quite sound.

REVISED PRELIMINARY PLANT SCALE QUANTITATIVE
FLOW SHEET FOR THE PRODUCTION OF CUPROUS OXIDE
FROM CALUMET AND HECLA MIXED OXIDES

Calculations by:

E. A. Blaine

Report written by:

E. A. Blaine

Approved for the Development
Laboratory by:

AR Bozarth

Date 4/4/97

Copy No. 11

REVISED PRELIMINARY PLANT SCALE QUANTITATIVE
FLOW SHEET FOR THE PRODUCTION OF CUPROUS OXIDE
FROM CALUMET AND HECLE MIXED OXIDES

INTRODUCTION

Attached is a laboratory projected to plant scale quantitative flow sheet for the production of cuprous oxide from Calumet and Hecla mixed oxides. No pilot scale work has been done upon this process. The process is based upon bench scale experiments in glassware by J. O. May of the Research Laboratory.

The plant is designed to produce 200,000 lbs. of Cu_2O per month using as a raw material Calumet and Hecla mixed oxides, 80% Cu_2O and 20% CuO .

DESCRIPTION OF THE PROCESS

Milling and Classifying Operation

The mixed oxides are fed into the Hydrorake Classifier by means of a Hardinge A Feeder, capable of handling 11,920 lbs. (dry basis) of oxides per day. The classifier is 10 ft. in diameter. The coarse particles are raked out of the bowl classifier and sent to the Hardinge continuous conical ball mill (size, 4.5 ft. in diameter and 2 ft. long). The milled product is sent to the Hydrorake classifier, where the coarse material is again returned to the mill. The mill is to be sealed to the atmosphere at both ends, or an inert gas is to be passed over charge to prevent oxidation of the cuprous oxide.

The Dorr thickener, 6 ft. in diameter, receives the fines from the classifier and concentrates it to 60% solids. The water from the thickener drops into a sump from which it is pumped back

into the classifier.

The slurry from the thickener is pumped into a trough which can be swung to any one of the three reaction tanks.

Sulfuric Acid Storage and Dilution

The sulfuric acid used in the process is 66 deg. Be (93%), and is stored in a steel tank. The amount required is 3136 lbs. per day, which is diluted to 48%. The dilution tank is an 8' x 8' lead lined wood tank, having a side-mounted agitator. A lead cooling coil would be necessary.

The 48% sulfuric acid is then pumped into an 8' x 8' wood storage tank lead lined. From there it is pumped into the reaction tank.

Sulfuric Acid Leaching

The sulfuric acid leaching tanks are of wood, 10 ft. in diameter and 10 ft. high. A sweep agitator is used to mix the slurry. A cooling coil of lead is necessary; the solution is not to rise above 40 deg. C.

The 60% slurry from the thickener, containing 11,900 lbs. of mixed oxides and 7,920 lbs. of water, flows into the tank through the trough. Simultaneously, 6,120 lbs. of 48% sulfuric acid is added. The pH of the solution must be rigidly controlled; it must be within 2.5-3.0. The reactants must be held there for some time, estimated to be about 8 hours.

The temperature of the resulting mixture must be controlled; it must not rise above 40 deg. C. It can be controlled by 1) circulating cooling water through a lead coil, 2) control the rate of feed

of the reactants and 3) the dilution of the sulfuric acid to some value so that at a specified rate of feed the temperature will never rise above 40 deg. C. Any one of the above methods, or any combination, can be used to control the temperature.

Before the reactants are added to the tank, there must be a dilute copper sulfate solution present. The solution is 1,650 lbs. containing approximately 206 lbs. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. It hasn't been determined, but it may be possible to start the reaction with 1) plain water, 2) a portion of the previous batch, 3) a smaller amount of copper sulfate solution.

Three tanks are necessary: one tank is being filled, one is being emptied and in the third the cupric oxide is being dissolved.

Filtration of the Cuprous Oxide After Leaching

The cuprous oxide slurry is transferred to a vacuum filter. A rubber lined diaphragm pump and lead or rubber lined pipe lines are recommended to transfer the slurry to the filter.

The vacuum filter is estimated to be 3 ft. in diameter and 2 ft. long and can be of rubber, wood or lead construction. No tests were run to determine the feasibility or capacity of this type of filter.

The filtrate, 14,191 lbs. of solution, containing 7,631 lbs. of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is transferred to a 12' x 12' wood storage tank. The tank must be heated and have a side mounted agitator.

The solution from here is pumped to the COCS production department, which is to be charged with 7,425 lbs. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ per day. It is necessary to recirculate copper sulfate solution containing

206 lbs. of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ to the reaction tank.

The cake from the vacuum filter is transferred to the wash tanks by means of a conveyor.

Cuprous Oxide Washing

The cuprous oxide cake is conveyed to one of the three wash tanks. Three wash tanks are necessary: one tank is being filled, one is being emptied and in the third the cuprous oxide is being washed.

The tanks are 8' x 8' wood tanks, having a sweep agitator. The oxide is washed by decantation. The amount of water used and number of washings are yet to be determined.

The filtrate from this step can be sent to the copper sulfate storage or to the sewer. The wash water at the end of the washing step may contain a negligible amount of copper.

The last wash is to contain 23.8 lbs. mineral oil. The effect of any oil residue remaining in the tank may adversely affect (this has not been checked) the washing of the next batch. In which case, the oil addition will have to be done in a separate tank.

The thick slurry from these tanks is then transferred by means of a neoprene diaphragm pump to a second vacuum filter, 3 ft. in diameter and 2 ft. long. No work has been done to determine the feasibility or capacity of this type of filter. The filtrate is discarded. The filter cake is transferred to the vacuum drier.

Drying the Cuprous Oxide

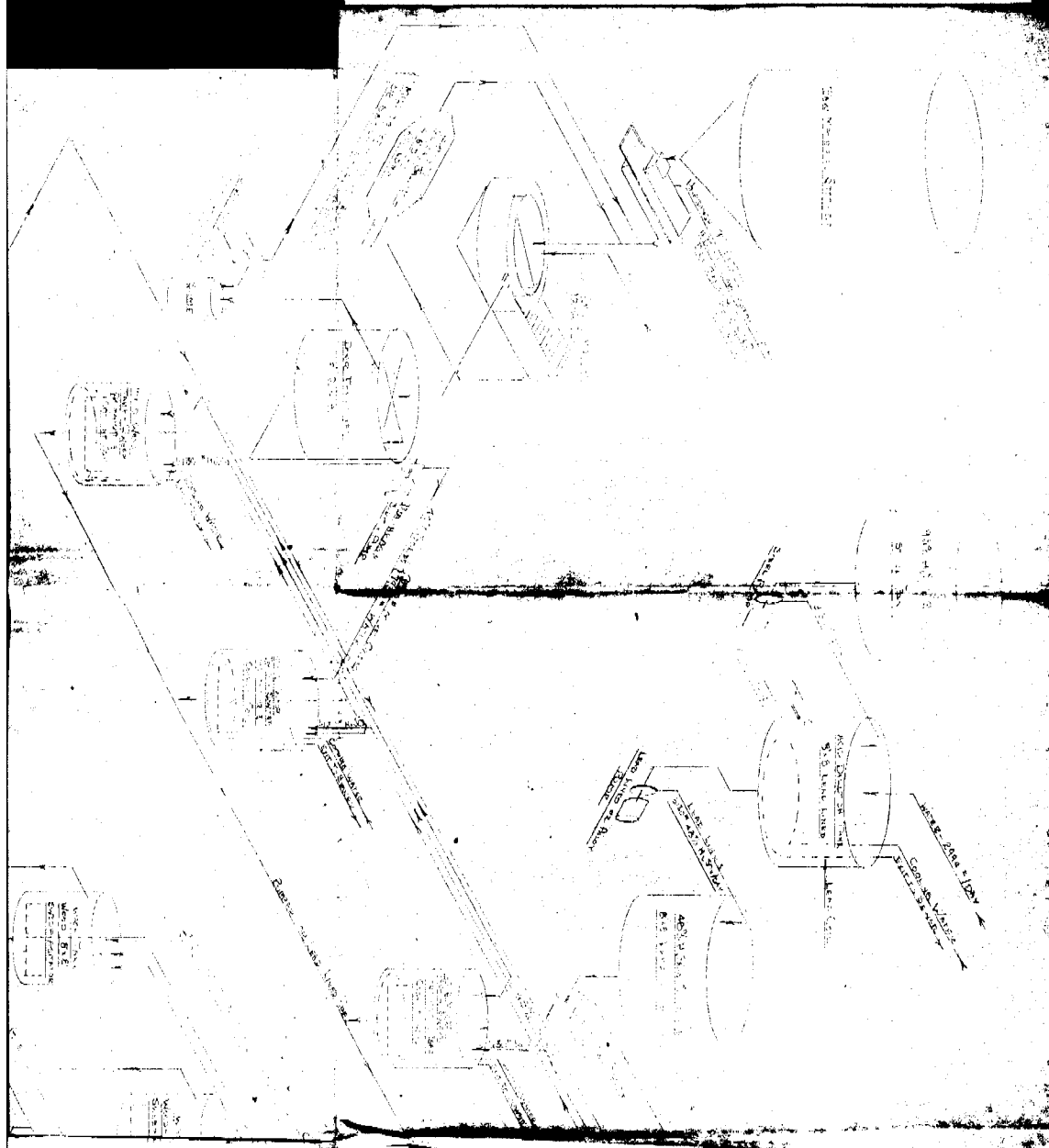
The oil coated cuprous oxide from the vacuum filter is conveyed to a Devine No. 4 vacuum rotary drier. The rotary is 4 ft. in diameter and 12 ft. long and is to be steam heated to 80-120 deg. C.

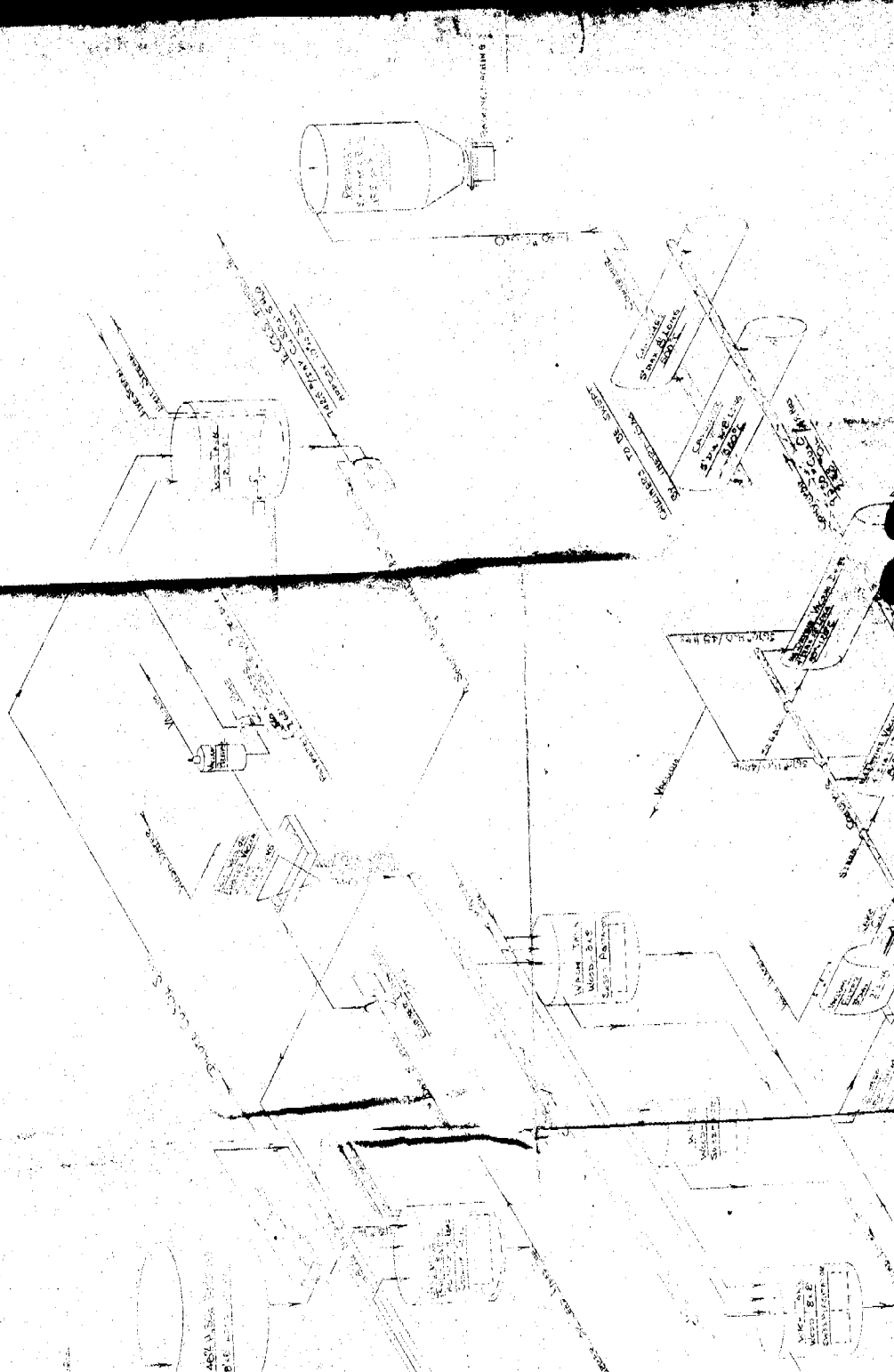
Two driers are needed, one to be filling while the second is drying the cake and being emptied. It is assumed that a 24-hour filling, drying and unloading cycle is correct.

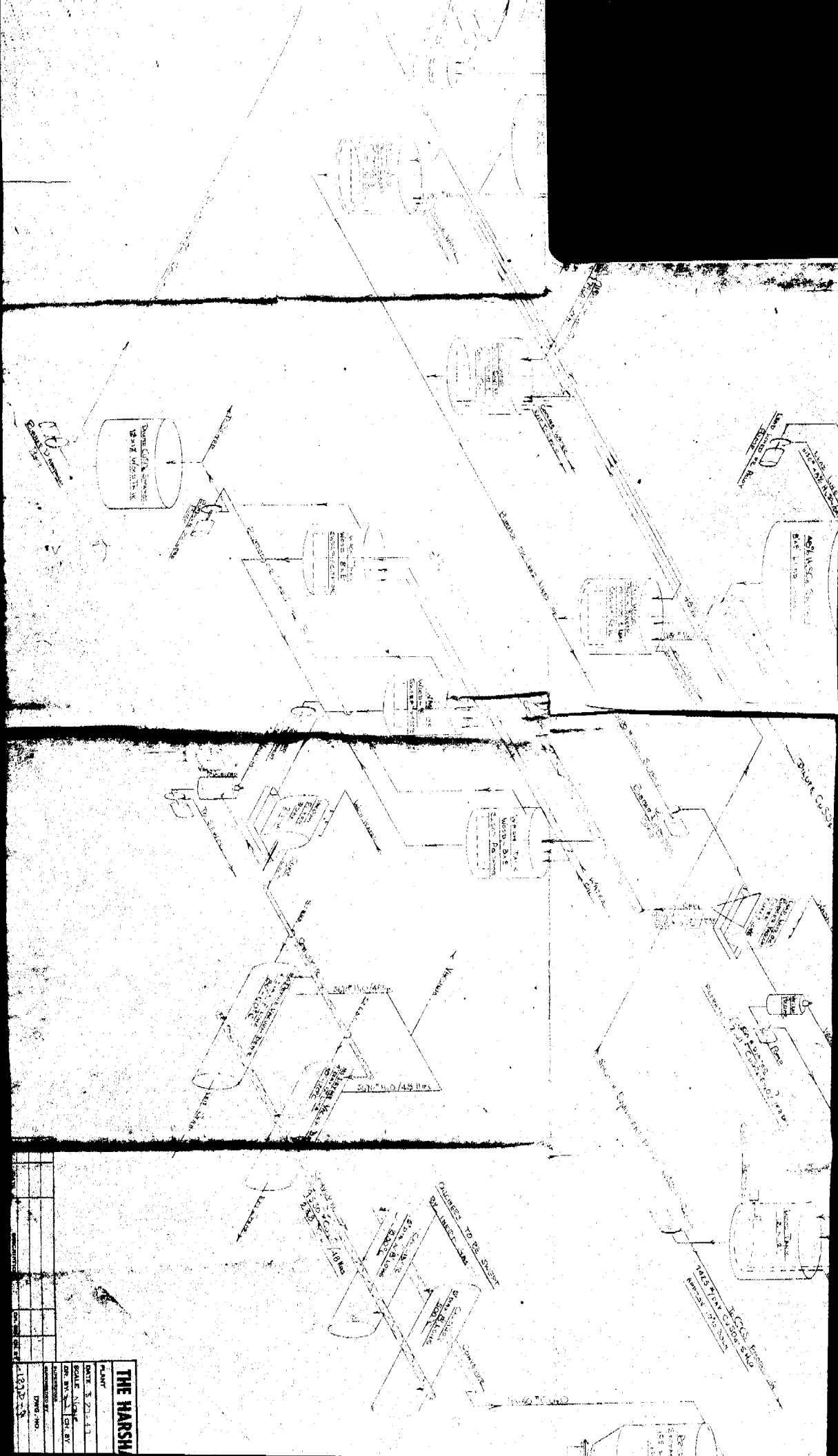
To obtain the best possible product, a calcination step is necessary. The product prior to calcination may meet the standards set by sales. The calciners are 5 ft. in diameter and 8 ft. long and to be heated to 500 deg. C. The charge is to be heated to the required temperature and cooled to room temperature under an inert atmosphere. It is assumed that charging, calcining and unloading the calciner is on a 24-hour cycle.

The dry cuprous oxide is unloaded into a screw conveyor and transferred to a packaging machine.

In conclusion, the process has been based upon the work done by the Research Laboratory and upon which no work has been done by the Development Department.







THE HARSH PLANT DATE: 3-22-11 DRAWN BY: [Signature] CHECKED BY: [Signature] DWG. NO.: 1002-3	
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4 → CUPRIC OXIDE PLANT

(Weight of CUPRIC OXIDE = 144^{lb} per unit)

MS-002 Box 34

Folder 29

DRAWINGS

FLOW SHEET	PART	REQ'D	DETAILS FOR SUPPORTS	ARRGT	REQ. NO	DELIVERY
COPPER OXIDE	STORAGE BIN	✓	EXISTING	1077-1		
	STORAGE BIN OUTLET	✓	STEEL WELDED - C+H (ELS-GWM)	10921	10921	13186 SEPT. 22
ELEVATOR	CASING, BELT & BUCKETS	✓	EXISTING #10758-8-9. - MAKE 25'-0" ϕ S.	10912		13175 SEPT. 15
	SPEED REDUCER	✓	17 1/2 to 1 WB40 LINK BELT (FROM COCS)			ON HAND (REQ. 13138)
	SPROCKETS & CHAIN	✓	1-60T, 1-45T, 1-RC60 ROLLER CHAIN - LINK BELT	10912	10912	13176 REC'D (REQ. 13166)
	MOTOR	✓	2 HP - 750 RPM - C+H #2184			ON HAND - CLE-OK.
	DRIVE UNIT SUBBASE	✓	STEEL WELDED - C+H (W.W)	10912-1	10912	13176 SEPT. 15
	ELEVATOR & DRIVE SUPPORTS	✓	" " " (W.V.C + GWM)	10912	10912	13175 SEPT. 15
FEED HOPPER	FEED HOPPER	✓	STEEL WELDED - C+H (ELS)	10914	10908	13183 SEPT. 22
	BIN-DICATOR	✓	BIN-DICATOR CO - DETROIT			EE 14765 SEPT. 30
FEEDER	JEFFREY TRAILOR FEEDER		C.T. DE HAAS		10908	13133 late Nov. { De Haas telegram 11/20/49
	FEEDER SUPPORT	✓	STEEL WELDED - C+H (ELS)	10909-4	10908	13182 SEPT. 15
FURNACE	HERRESHOFF FURNACE	✓	ON HAND - SMELTER		10908	ON HAND
	H. FURN. SUPPORT	✓	STEEL WELDED C+H (ELS)	10909	10908	13182 SEPT. 15
	H. FURN. OIL BURNER	✓	NAT'L. AIR OIL BURNER CO	-	-	13205 RUSH order 10/17/49
	H. FURN. DRIVE	✓	ON HAND - SMELTER	-	-	ON HAND
SCREW CONVEYOR	W.C. CONVEYOR BOX	✓	STEEL WELDED - C+H (ELS & GWM)	10916	10908	13181 SEPT. 15
	FLIGHT	✓	ON HAND - SMELTER (A.P. LEB)	10916		13181 SEPT. 15
	DRIVE UNIT	✓	FROM DORR CO FILTER (CALUMET MILL)	10909	10908	13177 ON HAND
	MOTOR	✓	" " " " 1 1/2 HP - GH #1258			
	DRIVE - SUB BASE	✓	STEEL WELDED (ELS)	10909-2	10908	13182 SEPT. 15
PULVERIZER	MIKRO PULVERIZER	✓	PULVERIZING MACH'Y CO			13132 REC'D
	MAIN DRIVE MOTOR	✓	5 HP LOUIS ALLIS - 1425 RPM - C+H #2196	10929	10929	EE 14719 REC'D
	FEED DRIVE MOTOR	✓	1/4 HP 1425 RPM - C+H #			EE 14726
	DETAILS & GEN'L ARRG'T.		MOTOR BASE ETC.			
STORAGE BIN	5 TON BIN	✓	STEEL WELDED - C+H (ELS)	10901		13179 SEPT. 15
	BIN SUPPORTS	✓	" " (W.V.C)	10901		13179 " 15
SCREW FEEDER	SCREW FEEDER		C.T. DE HAAS		10729-3	13135 NOV. 22 A.B.T. DE HAAS NOV 20/49
	SPEED REDUCER	✓	#12 W. WORM GEAR 7 1/2 to 1 - FODTE BROS			13134 REC'D
	MOTOR	✓	5 HP G.E. MOTOR - 720 RPM - C+H #2197			EE 14719 REC'D
	V-BELT DRIVE			13186	10928	13193
	DRIVE DETAILS & ARRG'T			10928		

REV. NOV. 15, 1949
Sept. 18-1949
OCT. 20-49
P.H.O.

LAW OFFICES

HOFGREN, WEGNER, ALLEN, STELLMAN & MCCORD

20 NORTH WACKER DRIVE

CHICAGO 60606

TELEPHONE
FINANCIAL 6-1630
AREA CODE 312

AXEL A. HOFGREN
ERNEST A. WEGNER
JOHN REX ALLEN
WILLIAM J. STELLMAN
JOHN B. MCCORD
BRADFORD WILES
JAMES C. WOOD
STANLEY C. DALTON
RICHARD S. PHILLIPS
LLOYD W. MASON
TED E. KILLINGSWORTH
CHARLES L. ROWE
JAMES R. SWEENEY

THOMAS A. STANSBURY
J. R. STAPLETON
WILLIAM R. MCNAIR
JOHN P. MILNAMOW
DILLIS V. ALLEN

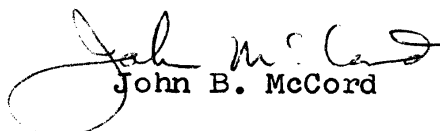
January 18, 1965

Mr. A. E. Petermann
Calumet & Hecla, Inc.
122 South Michigan Avenue
Chicago 3, Illinois

Dear Mr. Petermann:

As requested in your letter of January 12th, we have obtained and are enclosing copies of the 3 patents involved in the recent assignment from Lake Chemical Co. to Calumet & Hecla.

Yours very truly,


John B. McCord

JBM:js
Encls.

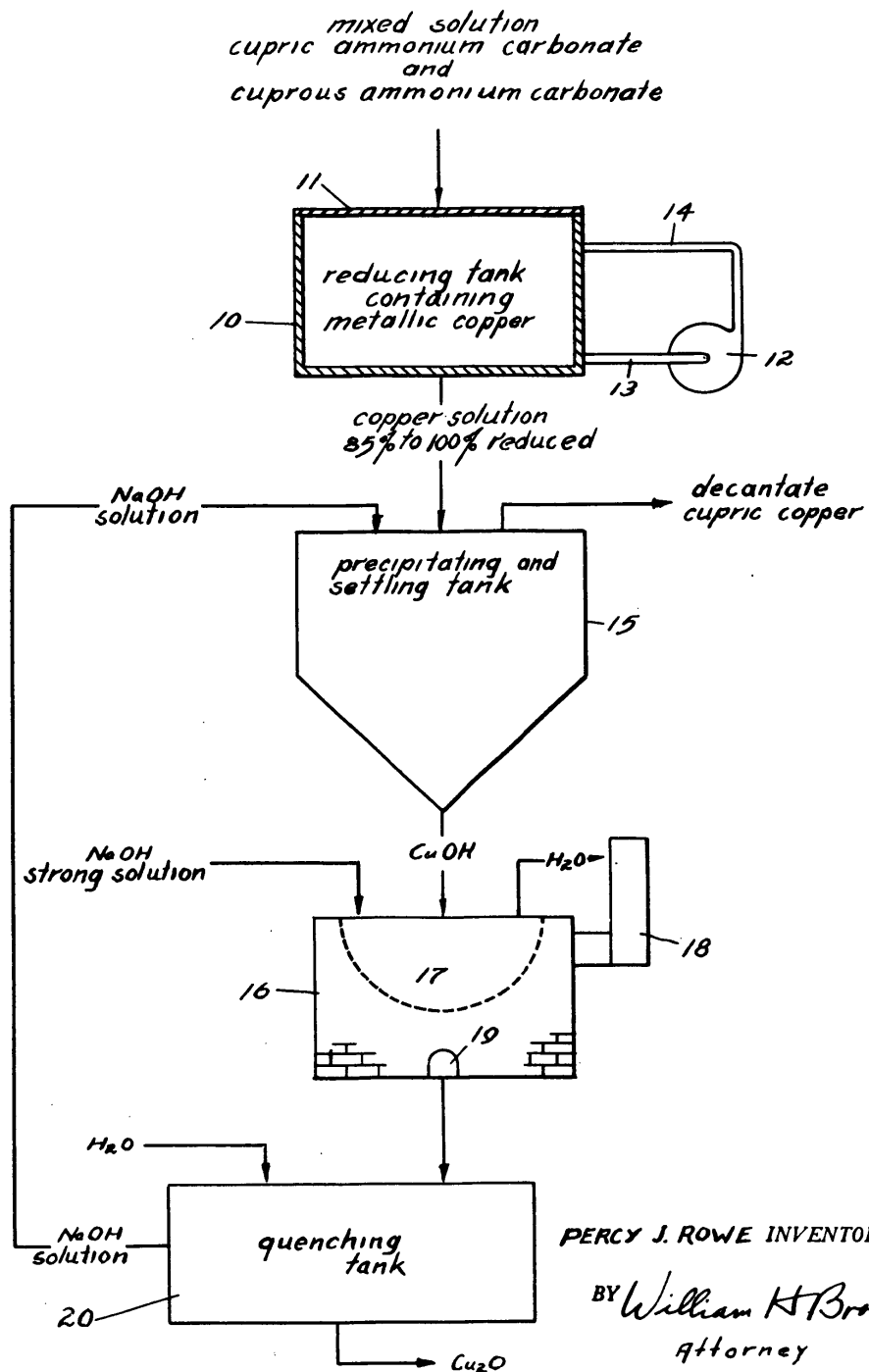
June 28, 1949.

P. J. ROWE

2,474,497

PRODUCTION OF CUPROUS HYDROXIDE AND CUPROUS OXIDE

Filed Feb. 16, 1946



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metallic copper in the form of scrap sheet, wire, clippings, or other form presenting a relatively large surface area. Circulation of the copper solution is induced in this tank by a pump or other mechanical means 12 communicating with the tank 10 through pipes 13 and 14. The net result of such treatment is the production of a copper ammonium carbonate solution containing 50 per cent or more of the dissolved copper in the reduced (cuprous) state. Although I prefer to work in the higher ranges of cuprous content (e. g. 85% to 99% or if found practicable, which is hardly likely, even 100% of the copper in cuprous form) the reaction progresses satisfactorily in the lower concentrations down to a minimum of 50 per cent. A solution of this type (low cupric content) might contain 40 grams per liter of CO_2 , 60 grams per liter of NH_3 , and 60 grams per liter of copper, the increase in copper over that in the starting solution being due to the dissolving of metallic copper by action of cupric copper during its reduction in the starting solution. Such a solution should contain from 30 to 70 grams per liter of CO_2 , 35 to 75 grams per liter of NH_3 , and 20 to 100 grams per liter of copper or even higher up to the limit of solubility of copper in said solution. This wholly or partially reduced copper solution from the first step in the process is then conveyed to a suitable closed vessel 15, preferably having a cone-shaped bottom. Prior to the introduction of the cuprous copper enriched solution, I introduce a solution of caustic soda (wherever caustic soda is mentioned herein, KOH might be used but caustic soda is preferred) into the tank in calculated amounts as previously described approximately those which are just sufficient to combine with the CO_2 content and precipitate all or nearly all of the cuprous content of the solution as a yellow precipitate of cuprous hydroxide (or hydrated cuprous oxide) but insufficient to precipitate any large quantity of cupric copper. Although I prefer to introduce the reduced copper ammonium carbonate solution into the caustic, the reaction proceeds satisfactorily when the solution of caustic soda is added to the solution of copper ammonium carbonates. The reaction between the caustic soda and the copper ammonium carbonate solution may be suitably carried out at room temperature, but some degree of heating, such as that resulting from the contact between the caustic alkali and the ammoniacal solution, or external heating, facilitates the rapid coagulation and separation of the precipitate. In either case, the precipitate is permitted to settle and the supernatant liquid is removed by decantation or other suitable means. The values in this liquor may be recovered as hereinafter stated. The yellow precipitate of cuprous hydroxide may be washed, in the absence of air insofar as practical, by any convenient method to remove from it essentially all sodium salts, ammonia, and cupric copper.

The resulting yellow cuprous hydroxide in the form of mud or thick slurry may be treated in this same vessel or transferred into other suitable equipment, such as a furnace 16 having a receptacle 17, a stack 18 and fire box opening 19, where additional caustic soda is added. The concentration of caustic is not critical, but concentrations of 50 per cent or more are preferred in order to reduce the period required to eliminate essentially all of the water. Heat is applied to effect evaporation of the water, and with increasing temperature the concentration of caustic is built up. When a temperature of approximately 200° F. is

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reached, the conversion from cuprous hydroxide to cuprous oxide begins, as evidenced by a change in the color of the slurry from yellow to red, and as further water is evaporated and the caustic concentration is increased, the reaction proceeds until at about 300° F. the conversion appears to have been completed. A temperature of 300° F. however, is not a critical upper limit, and heating may be continued further (with consequent increase in temperature) up to say 600° F. or even higher. Alternatively the conversion may be effected by prolonged heating at temperatures between 200° F. and 250° F. The cuprous oxides produced at different temperatures of conversion have somewhat different physical characteristics with respect to particle size, color, etc., but temperature does not appear to affect the cuprous oxide content nor the total reducing power.

After the cuprous hydroxide has been converted to the cuprous oxide, water may be added to prevent crystallization of the caustic alkali, and the material transferred to any suitable vessel 20 where the cuprous oxide is washed free from caustic. It is then filtered, and dried by any suitable method.

My preference is always to work with solutions in which the greater part of the copper is in the cuprous form, and when solutions containing more than 85% of the copper in the cuprous form are employed the product is always of excellent quality. In cases where the solution contains only 50% or 60% of the copper in the form of cuprous ammonium carbonate, it is sometimes desirable to boil the final product in an excess of caustic soda to dissolve out the cupric oxide and thereby improve the product. It is, of course, preferable to avoid this step by treating the initial solution to convert the cupric ammonium carbonate to the corresponding cuprous compound. For example, note the following experimental results.

Table I

No.	Total Cu, Gm./L.	Per Cent Cuprous	Reducing Power of Product	Reducing Power of Product After Reboiling with NaOH
1.....	59	92	Per Cent 98.76	Per Cent
2.....	60.75	55	90	98

In another series of experiments, sufficient caustic was added during the initial precipitation to precipitate all the copper, both cuprous and cupric.

Table II

No.	Total Cu, Gm./L.	Per Cent Cuprous	Reducing Power of Product	Reducing Power of Product After Reboiling with NaOH
1.....	60.7	55	Per Cent 56.5	Per Cent 58.4
2.....	44.8	35.5	35.6	

In each of the above tables, reducing power is expressed in percentage and is compared with pure cuprous oxide as 100%. The first two columns refer to concentrations in the solution from which the hydroxide is precipitated. The last columns indicate the result when the oxide was reboiled with an excess of caustic soda. The amount actually used was about equi-molecular with the Cu_2O in the product.

From these tables it may be concluded that the caustic not only converts the initial precipi-

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tate (CuOH plus $\text{Cu}(\text{OH})_2$) to oxides but also acts as a solvent for the cupric copper contained in the precipitate. This effect of dissolving cupric copper compounds takes place to some extent when the process is carried out under normal, favorable conditions; that is, during the conversion of the hydroxide to the oxide, and this, as well as the effect of selective precipitation of cuprous hydroxide, contributes to the excellence of the product.

The recovery of the values from the decanted liquors containing cupric copper, ammonia, caustic, and carbon dioxide, is not essential to the operation of my process, but is economically desirable. This recovery might be accomplished by various known methods; such as, distilling the ammonia, precipitating the copper as cupric oxide or carbonate, and evaporating the mother liquor to obtain soda ash. These products are not all immediately returnable to my process, but may be utilized in related industry and it is possible to utilize the caustic liquor from the conversion of the hydroxide to Cu_2O in precipitation of further quantities of hydroxide.

The following specific example will serve to illustrate the invention:

Example

One cubic meter of copper ammonium carbonate solution was prepared containing 35 grams per liter total copper, of which 30 grams per liter was in the cupric state and 5 grams per liter in the cuprous state. The solution contained 40 grams per liter of CO_2 and 60 grams per liter of NH_3 . This volume of copper ammonium carbonate solution was then introduced into a cylindrical tank 10, having a capacity of $1\frac{1}{2}$ cubic meters, which had been previously filled with copper wire scrap. After closing the tank to exclude essentially all air, the solution was circulated through the bed of copper by pumping in closed circuit 12, 13, 14, for 20 hours at room temperature. At the end of the 20 hour period, the solution assayed 55 grams per liter cuprous copper, 5 grams per liter cupric copper, 40 grams per liter CO_2 , and 60 grams per liter NH_3 . The solution was then pumped into an adjacent tank 15 having a capacity of $1\frac{1}{4}$ cubic meters and constructed with a cone-shaped bottom, into which a solution of 50 per cent caustic soda, containing 185 pounds of NaOH (76% Na_2O), had been previously introduced. In order to intimately mix the copper-bearing solution with the caustic solution, and to avoid any oxidation, the prepared copper ammonium carbonate solution was introduced near the bottom of the cone under pump pressure. Precipitation of the yellow cuprous hydroxide occurred almost instantaneously, and after all of the copper ammonium carbonate solution had been introduced, was allowed to settle for 8 hours.

The supernatant liquid above the precipitate was drawn off, and assayed $4\frac{1}{2}$ grams per liter of copper, 54 grams per liter NH_3 , and an undetermined quantity of sodium carbonate. This solution was treated in an evaporator, where the NH_3 was expelled and the gas condensed as aqua ammonia; the copper was recovered as oxide and the remaining solution evaporated for the recovery of sodium carbonate.

The cuprous hydroxide slurry in the cone of the reaction tank was washed with 200 gallons of water by introducing the water under pressure through the bottom of the cone. The precipitate was again allowed to settle for 8 hours, after

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which the supernatant liquid above the precipitate was drained off and discarded. The resulting cuprous hydroxide weighed 150 pounds. The washed cuprous hydroxide slurry was introduced into a cast iron caustic pot 17, into which had been added 150 pounds of flake caustic soda (76% Na_2O). The pot was supported in an oil-fired, well-type furnace 16 and gradually heated for about one-half hour to avoid excess frothing and boiling. During the initial heating the greater part of the ammonia was expelled. When the solution reached a temperature of 250°F . conversion of the cuprous hydroxide to the cuprous oxide became evident as the color changed gradually from yellow to red. The temperature was gradually increased over a period of 2 hours to a maximum of 350°F ., although the reaction appeared to be complete at 300°F . The slurry was then diluted with water to approximately 50 per cent caustic and removed to a cone settling tank. The cuprous oxide was allowed to settle for 2 hours, after which the clear caustic solution was decanted from the precipitate and placed in storage for further use. The cuprous oxide precipitate was then washed free of solubles, filtered, and dried. The red cuprous oxide recovered weighed 136 pounds and was of a bright red color with an extremely fine particle size.

Having thus described my invention, what I claim is:

1. A process comprising the steps of mixing with a caustic alkali of the class consisting of sodium and potassium hydroxides an aqueous, ammoniacal copper carbonate solution, said solution containing per liter on an analytical basis from 30 to 70 grams CO_2 , from 35 to 75 grams of NH_3 and from 20 grams per liter to saturation of copper, said copper being present in cuprous form in a major amount but also comprising a substantial amount thereof in cupric form, the caustic alkali being present in such concentration and such amounts that cuprous copper is precipitated as cuprous hydroxide and substantially all of the cupric copper remains in solution, and separating the precipitate of cuprous hydroxide from the reaction mixture.

2. A process as defined in claim 1 further characterized in that the amount of caustic alkali is from 0.8 to 1.5 times the molecular equivalent of the CO_2 content of the solution.

PERCY J. ROWE.

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UNITED STATES PATENT OFFICE

2,474,497

PRODUCTION OF CUPROUS HYDROXIDE
AND CUPROUS OXIDEPerry J. Rowe, Hubbell, Mich., assignor to Lake
Chemical Company, Calumet, Mich., a corpora-
tion of Michigan

Application February 16, 1946, Serial No. 648,153

2 Claims. (Cl. 23-147)

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This invention relates to the production of cuprous oxide and has for its principal object to provide a process for recovering cuprous oxide from solutions containing copper ammonium carbonate.

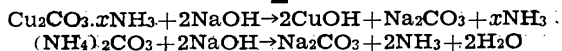
Prior to my invention a number of methods have been proposed for the production of cuprous oxide but so far as I am aware none of these has proved completely satisfactory and no one has to my knowledge disclosed a process suitable for recovering cuprous oxide from the commercially available copper solutions which I propose to employ.

I have now discovered a process for producing cuprous oxide (or, optionally, cuprous hydroxide) from solutions containing copper in the form of cuprous ammonium carbonate or both cuprous and cupric ammonium carbonate. I preferably treat the solution (usually mixed because of the difficulty in obtaining a solution in which the copper is entirely cuprous) if it contains more than about 15% of the copper in cupric form, to reduce the amount of cupric copper and increase the amount of cuprous copper in solution. I have found that I am able to precipitate a cuprous compound which I believe to be cuprous hydroxide (CuOH) from solutions containing 50% or more (preferably 75% or more) of the copper in solution in the form of cuprous ammonium carbonate (the remainder being in the form of cupric ammonium carbonate) and without precipitating an excessive quantity of cupric hydroxide, and by a separate step to convert the cuprous hydroxide into cuprous oxide and dissolve out a part of the small proportion of Cu(OH)_2 precipitated.

I first contact an aqueous solution containing cuprous and cupric ammonium carbonates in suitable concentrations with metallic copper in the absence of air whereby to obtain a solution wherein at least 50%, and preferably 75% or more, of the copper is present as cuprous copper and then treat such solution with an amount of alkali sufficient to precipitate substantially all the cuprous copper in solution but insufficient to precipitate any substantial proportion of the cupric copper. (The reduction of cupric copper to cuprous copper may be omitted if the desired proportion of cuprous copper is already present in the starting solution). I then convert the precipitate to oxide by treatment with strong caustic.

The amount of alkali required for the preferential precipitation step can be determined by calculation. Thus, the cuprous ammonium carbonate and ammonium carbonate content of the mixed copper solution being known from experience with a closely controlled solution or by analysis, the stoichiometric quantity can be calculated according to the following reactions:

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Less than the amount of caustic thus calculated will give satisfactory results, that is, will precipitate substantially all the cuprous copper, and a greater quantity can be tolerated, that is, will not precipitate any great quantity of cupric copper. The amounts of cupric copper precipitated when greater amounts of caustic are employed depend not only upon the concentration of cuprous ammonium carbonate and ammonium carbonate but also upon the concentration of cupric copper so that for solutions containing above 85% of the copper in cuprous form, it is possible to utilize greater proportions of caustic soda without precipitating a great deal of cupric copper. In any case, the practical limits are more or less a matter of choice since the considerations which actually determine the limits are on the one hand the amounts of cuprous copper which it is decided can be allowed to remain unprecipitated and on the other hand the amounts of cupric copper which can be allowed to be precipitated. I prefer to use from 0.8 to 1.5 times the calculated proportion of caustic required by the above formula. Stated in terms of the final product, I prefer to use from 1 to 2 pounds of caustic soda (or the molecular equivalent of KOH) for each pound of Cu_2O produced.

In the accompanying drawings the figure is a flow sheet illustrating the preferred embodiment of the invention.

The initial copper ammonium carbonate solution preferably normally is one containing approximately 40 grams per liter of CO_2 , 60 grams per liter of NH_3 , and 35 to 40 grams per liter of copper, a large part of which may be in the oxidized condition; i. e., cupric ammonium carbonate. A solution meeting these general requirements is now produced commercially in a process for dissolving copper from various types of copper-bearing materials. This commercial composition may be expected to vary within limits as follows: CO_2 from 30 to 70 grams per liter; NH_3 from 35 to 75 grams per liter; and copper from 10 to 50 grams per liter. Any of these solutions, and others of similar composition, however produced, are suitable as starting solutions for my process, the only restriction being that they must be sufficiently low in copper to permit the subsequent addition of copper in amounts sufficient to reduce a large part of the cupric copper initially in solution to cuprous copper before this reduction is inhibited by the limited solubility of copper in solution.

As shown in the accompanying flow sheet, the copper ammonium carbonate starting solution is run into a closed tank or vessel (provided with a cover 41 whereby to exclude air) containing

UNITED STATES PATENT OFFICE

2,474,533

PREPARATION OF CUPROUS OXIDE

Lawrence C. Klein, Hubbell, Mich., assignor to
Lake Chemical Company, Calumet, Mich., a
corporation of Michigan

No Drawing. Application February 26, 1947,
Serial No. 731,051

6 Claims. (Cl. 23—147)

1

This invention relates to the preparation of cuprous oxide and more specifically to the separation of cupric oxide from a mixture of cuprous and cupric oxides.

It has long been known that cupric ammonium carbonate solutions containing an excess of ammonium carbonate, will dissolve metallic copper forming cuprous ammonium carbonate. Theoretically, it would be possible for a solution containing one pound of copper as cupric ammonium carbonate, to dissolve one pound of metallic copper, and form, in solution, two pounds of copper as cuprous ammonium carbonate. In practice this rate of solution is never attained, but by exercising painstaking care it can be very nearly approached. This solution, containing most of the copper in the cuprous state, on being distilled to recover the copper value as the oxides, and, barring any oxidation in distilling, yields an oxide which is a mixture of cuprous and cupric oxides, the proportions of each being approximately the same as the cuprous to cupric copper ratio in the solution before distilling.

For several years attempts have been made at various times to produce a commercial grade of cuprous oxide by the distillation of solutions of copper ammonium carbonate that had been highly reduced to the cuprous state by contact with metallic copper. A satisfactory product has never been made by this method.

I have now found, that if the mixed oxide produced by the above method be treated with certain water-soluble organic acids or water solutions thereof (for example, acetic acid) under controlled conditions, the cupric oxide will be dissolved forming the cupric salt of the acid used, and leave undissolved, or practically so, the cuprous oxide. The cuprous oxide may be separated by filtering, washed free of acid and salts, and dried. The cupric salt may be recovered by conventional crystallization processes. The excess organic acid may be recovered by condensing the vapors evolved in concentrating the filtrate for crystallization, or by diluting it and placing it on fresh mixed oxide and allowing it to dissolve cupric oxide until practically all of the acid is consumed in forming the copper salt.

As commercially practiced, the solution circulating in the leaching system is an aqueous solution of copper ammonium carbonate, with an

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excess of ammonium carbonate. The copper in this solution when used for leaching is oxidized to the cupric state by air in an absorber tower. This solution is then percolated through tanks containing copper-bearing materials. The cupric ammonium carbonate solution dissolves metallic copper, thereby becoming reduced to form cuprous ammonium carbonate. Theoretically, it is possible to dissolve one pound of copper metal for every pound of copper already in solution as cupric ammonium carbonate, but this limit is never completely attained. A portion of this rich solution from the tanks, containing copper in amount equivalent to the metallic copper which was dissolved, is distilled to decompose it into copper oxides, ammonia and carbon dioxide. Ammonia stills are used for this purpose, steam entering at the bottom, and solution entering at the top. The mixed copper oxides are discharged at the bottom with waste liquor (water with a trace of ammonia). The ammonia and carbon dioxide with water vapor go to a condenser where they are cooled to form an ammonium hydroxide-ammonium carbonate solution (distillate). The undistilled portion of the rich solution, and the distillate are combined, water, carbon dioxide and aqua ammonia are added as required and this is oxidized with air to make up a new leach solution.

A typical leaching solution would contain 10 to 60, preferably 30 to 40 grams per liter, of copper (90 to 100% oxidized—that is, in the cupric state); 30 to 100, preferably about 60 grams per liter, of ammonia; and 20 to 60, preferably about 40 grams per liter, of carbon dioxide. The rich solution might in a usual case contain from 20 to 100 grams per liter of copper, with about the same concentrations of ammonia and carbon dioxide as in the leach solution. The amount of copper dissolved determines the amount of copper in the cuprous and the cupric state in the rich solution.

In practice it is possible to obtain solutions containing up to about 95 per cent of the copper in the cuprous state, which on distilling yield a mixed oxide containing up to about 92 per cent of the copper as cuprous oxide, the balance being cupric oxide. This oxide is not stable unless it is immediately dried after filtering, as the presence of moisture and a trace of ammonia prob-

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ably accelerates the gradual oxidation of the cuprous oxide to cupric oxide. To prevent this oxidation, the oxide, after filtering, is immediately dried and ground in a hammer-mill with flash drier apparatus. The cuprous oxide content of the dried oxide changes to cupric oxide but slowly, thus being suitable for various commercial purposes, and it is this oxide which, unless otherwise stated, has been used in preparing cuprous oxide of a commercial grade by dissolving out the relatively small amount of cupric oxide with organic acid or solutions of organic acids. Other mixtures of cuprous oxide and cupric oxide containing predominantly cuprous oxide can be successfully treated, suitable mixtures containing at least one mol of Cu_2O for each mol of CuO . I prefer to treat mixtures of higher Cu_2O content such as those indicated above containing 70% or more by weight.

I have found that acetic acid, and various strength water solutions of acetic acid will dissolve cupric oxide from mixtures of cupric oxide and cuprous oxide leaving most of the cuprous oxide unattacked. The cuprous oxide is but slightly affected by dilute solutions of acetic acid, but considerably more so in more concentrated solutions, and in glacial acetic acid, the action of concentrated acetic acid on cuprous oxide being to precipitate one-half of the copper as finely divided copper and to dissolve the other half as cupric acetate. Practical strengths of solutions are from 5 to 50 mols of H_2O per mol of acid, anhydrous basis. I prefer to use solutions of from 10 to 20 per cent (by weight) acetic acid in the process, this being optimum for fast dissolution of the cupric oxide and in excessive attack of cuprous oxide by the acid. These strengths are based upon the idea that such solutions will be added to the dry oxide mixtures. Adding part or all the water to the oxide mixture and then adding a stronger acid solution is an equivalent procedure.

Although the cupric oxide is dissolved and a satisfactory grade of cuprous oxide may be made by allowing the reaction to proceed at room temperature, I prefer to perform the treatment at from 70° C. to the boiling point of the solution. This greatly accelerates the dissolving reaction, gives a cuprous oxide product having brighter color, and increases the solubility of the cupric acetate in the solution so that less volume of solution is required. The solution in this case must be separated from the product while hot to prevent crystallization of the cupric acetate which would occur on cooling.

The amount of acetic acid necessary to treat a given amount of mixed oxide should be the amount necessary to combine with all of the cupric oxide present, plus an excess of at least 20 per cent. I prefer to use an excess of from 100 to 200 per cent or more to produce a good grade of cuprous oxide in the minimum time. The excess acetic acid also assures the recovery of the normal cupric acetate from the liquor. The excess acid may then be recovered in one of two ways: (1) By condensing the acid when the cupric acetate solution is concentrated by evaporation; and (2) by diluting the solution with water and applying it on fresh mixed oxide to allow the excess acid to dissolve more cupric oxide until it is practically all consumed in forming cupric acetate.

The volume of solution used for the solution of the cupric oxide is of importance in that enough solution must be used to retain in solution all of

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the cupric acetate that is formed; otherwise the cupric acetate will start to crystallize, and on filtering will contaminate the cuprous oxide and prove difficult to wash out. This can be overcome by diluting the acid liquor with water near the end of the reaction should crystals start forming in the mixture.

Other organic fatty acids were used in the same manner as acetic acid to determine whether they had the same effect in preferentially dissolving out the cupric oxide from cuprous and cupric oxide mixtures. Those used were formic, propionic, butyric, caproic, caprylic, and lauric. While it was found that all of these acids dissolved cupric oxide quantitatively before reacting with cuprous oxide and this latter reaction taking place only very slowly, there was a decrease in their effectiveness with an increase in the number of carbon atoms in the acid. Formic acid gave the best results, and lauric acid the least satisfactory. While it is possible to produce a fair grade of cuprous oxide from the higher acids with the necessary time and pains, it is felt that only the water soluble acids are of economic importance in producing cuprous oxide by this method; viz., formic acid, acetic acid, propionic acid, and butyric acid. Butyric acid is less desirable due to its lower solubility in water, and because of the lower solubility of its copper salt. To make cuprous oxide from mixed oxide with formic, acetic, or propionic acids, the procedure is identical except that the amount of acid necessary for solution of the cupric oxide will vary as the molecular weights of the acids.

Organic acids other than the fatty acids were also tried; namely, benzoic, oxalic, lactic, gallic, tartaric, succinic, citric, and salicylic. Of these lactic acid was found to produce a fine grade of cuprous oxide by dissolving out the cupric oxide. Oxalic acid had the same effect, but the product contained cupric oxalate which had to be removed. Tartaric acid showed the desired preferential solubility for cupric oxide, but proved less desirable because of a considerably slower rate of reaction.

The cuprous oxide produced by this method is a brick red to orange color, depending on the fineness of the particles. Most of the tests were made using oxide that had been dried and ground immediately after filtering, and so retained its high cuprous oxide content. Samples of freshly precipitated wet filter cake oxide were also used. It was found that with freshly precipitated oxide the cupric oxide dissolved out more rapidly and gave a product of slightly higher cuprous oxide content; however, it was a darker red color, presumably because of the larger particle size. On grinding this material it was found that the color could be changed from brick red to lighter red, or to orange, by finer grinding.

In practicing my invention, a solution of acetic acid (10 to 20%) is placed in a vessel equipped with a reflux condenser, agitator, and a source of external heat. To this the mixed oxide is added and the mixture agitated and heated, and allowed to reflux until a sample taken from it indicates that all of the cupric oxide has dissolved and the remaining cuprous oxide is brick red in color. Should any copper acetate crystals be apparent in the sample, water is added and the agitation and heating continued until the crystals have dissolved. The solution is then filtered hot (in the absence of air), washed with warm water until free of acid and cupric acetate, and finally with cold water to cool the oxide before

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discharging from the filter. The oxide is then dried at 60 to 70° C. in air, or preferably in a vacuum.

The filtrate is evaporated to concentrate the cupric acetate, the vapor being condensed to recover the excess acetic acid. The cupric acetate is recovered by crystallizing.

The following specific example will serve to illustrate the invention:

Example

One kilogram of mixed oxide, 83.95% total copper, 78.81% cuprous oxide, was treated as follows: A solution made up of 750 ml. glacial acetic acid (99.8% HAc) and four liters of water was added to the oxide, the mixture stirred and gradually heated to a maximum temperature of 64° C. and kept at this temperature for two hours with intermittent stirring. Toward the end of this period, crystals of cupric acetate started to form on the surface of the liquid, and water was added just sufficient in amount to keep the cupric acetate in solution. The oxide after two hours was a bright red color, and was separated from the liquor by filtering on a Buchner funnel, washed free of acetates with warm water, and dried in air at 60–70° C. The oxide produced had a total copper content of 87.63 per cent, with a total reducing power as cuprous oxide of 98.30 per cent. The filtrate assayed 13.68 grams per liter copper, or approximately 39 grams per liter cupric acetate. 812 grams of cuprous oxide was obtained, or 81.2 per cent of the original material. The filtrate from the test was evaporated and the cupric acetate separated by crystallizing. The crystals assayed 31.76 per cent copper.

Having thus described my invention, what I claim is:

1. In a process for producing cuprous oxide the steps of treating a mixture of cuprous oxide and cupric oxide containing at least one mol of Cu_2O for each mol of CuO with a low molecular weight, water soluble organic acid of the class consisting of formic, acetic, propionic, butyric, oxalic, tartaric and lactic acids in aqueous medium, the amount of acid being in excess of the theoretical required to react with the cupric oxide present by at least 20% and the amount of water being from 5 to 50 mols per mol of acid, anhydrous basis, until the cupric oxide has been dissolved and then separating the liquid portion of the reaction mixture from the Cu_2O which remains undissolved.

2. In a process for producing cuprous oxide the steps of treating a mixture of cuprous and cupric oxides containing at least 70% by weight Cu_2O with acetic acid in aqueous medium, the amount of acid being from 1.2 to 3 times the theoretical quantity required to dissolve the cupric oxide content of the mixture and the amount of water being from 5 to 50 mols of water for each mol of acid, until the cupric oxide has been dissolved and then separating the liquid portion of the reaction mixture from the Cu_2O which remains undissolved.

3. In a process for producing cuprous oxide the steps of distilling a mixture of cuprous ammonium carbonate and cupric ammonium carbonate in which the copper is not less than approximately 70% in the cuprous state at a temperature to remove ammonia and CO_2 , filtering the resulting mixture of cuprous and cupric oxides and drying the same immediately after filtering, treating the resulting mixture with a low molecular weight, water soluble organic acid of the class consisting of formic, acetic, propionic, butyric, oxalic, tartaric and lactic acids in aqueous medium, the amount of acid being in excess of the theoretical required to react with the cupric oxide present by at least 20% and the amount of water being from 5 to 50 mols per mol of acid until the cupric oxide has been dissolved and then separating the liquid portion of the reaction mixture from the Cu_2O which remains undissolved.

4. In a process for producing cuprous oxide the steps of treating a mixture of cuprous and cupric oxides containing at least 70% by weight Cu_2O with acetic acid in aqueous medium, the amount of acid being from 1.2 to 3 times the theoretical quantity required to dissolve the cupric oxide content of the mixture and the amount of water being from 5 to 50 mols of water for each mol of acid, until the cupric oxide has been dissolved and then separating the liquid portion of the reaction mixture from the Cu_2O which remains undissolved; the treatment with said acid being carried out at a temperature between 70° C. and the boiling point of the mixture and the separation of the solid and liquid phases being carried out at a temperature above that at which crystals of cupric acetate would form.

5. In a process for producing cuprous oxide the steps of contacting a mixture of cuprous oxide and cupric oxide containing from 70% to 92% of Cu_2O by weight with a low molecular weight, water soluble organic acid of the class consisting of formic, acetic, propionic, butyric, oxalic, tartaric and lactic acids in aqueous medium, the amount of acid being from 1.2 to 3 times the theoretical quantity to react with the cupric oxide present and the amount of water being a number of mols of water per mol of acid sufficient to produce a 10% to 20% solution by weight in the case of acetic acid, until the cupric oxide has been dissolved and then separating the liquid portion of the reaction mixture from the Cu_2O which remains undissolved.

6. The invention according to claim 5 wherein further during the first recited step the temperature is maintained between 70° C. and the boiling point of the solution.

LAWRENCE C. KLEIN.

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Oct. 10, 1950

P. J. ROWE

2,525,242

MANUFACTURE OF CUPRIC HYDRATE

Filed July 10, 1946

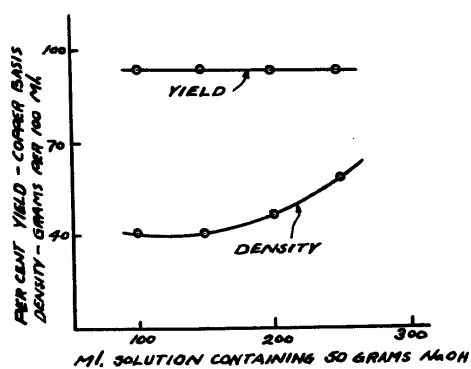


Fig. 1

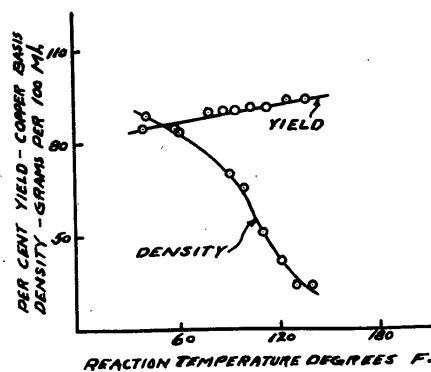


Fig. 2

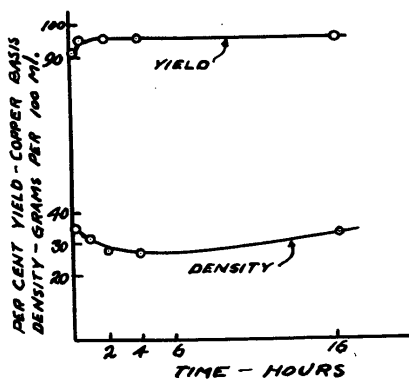


Fig. 3

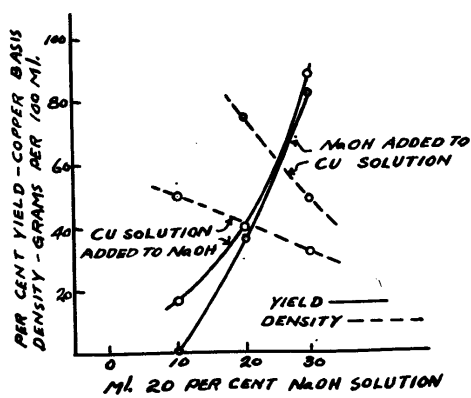


Fig. 4

PERCY J. ROWE INVENTOR.

BY William H. Brown

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from 80° F. to 140° F., a range from 100° to 120° F. being preferable. The length of time during which the precipitate is allowed to remain in contact with the mother liquor exerts a small but substantial effect on both the yield and the density. Standing for less than one hour, the yield is substantially lower than otherwise, and the apparent density is substantially higher than when the slurry is allowed to stand for a longer time. However, if the precipitate remains in the mother liquor too long, the apparent density again increases. The time of contact is not particularly critical, but when a product having an extremely low density is not required, the time of contact may be reduced to 15 minutes or less, but under these conditions the yield is slightly less, but where coarser crystalline material is required a longer period of contact is desirable, say, 1 to 8 hours. A very substantial lowering of density in a combination of conditions, making for satisfactory yield with respect to copper, can be obtained by adding the cupric ammonium carbonate solution to the sodium hydroxide solution instead of the reverse. The speed of addition of solution to alkali likewise exerts some effect on density and yield; viz., when 500 ml. of cupric ammonium carbonate solution containing 52.7 gpl of copper is added immediately to 150 ml. of 30% NaOH solution, stirred for 5 minutes, then allowed to settle for 30 minutes, the product has an apparent density of 46 grams per hundred milliliters; whereas, when the same volumes are added slowly over a period of 5 minutes, stirred and allowed to settle for 30 minutes, the apparent density of the product is 40 grams per hundred milliliters.

The copper for the preparation of the copper ammonium carbonate solution can be obtained from various grades of copper, either virgin or secondary, also copper clad and copper-containing materials including the cheaper grades of scrap. For some purposes the cheaper forms of scrap are entirely satisfactory while for products of high purity it may be necessary to use selected scrap or even pure metal. Some types of copper-containing materials may contain valuable metals other than copper which are insoluble in ammonium carbonate solution and accordingly are concentrated in a residue from which they may be readily recovered.

To prepare a cupric ammonium carbonate solution suitable for precipitating cupric hydroxide according to the invention I require first a suitable solution of ammonium hydroxide. I may use various concentrations but prefer to produce, by dilution of aqueous ammonia or by absorption of ammonia gas in water, a solution containing about 30 to 100 grams per liter of NH_3 . I then add CO_2 gas to such ammonium hydroxide solution either by bubbling in CO_2 gas or by mixing in a tower the ammonium hydroxide solution with the CO_2 gas as contained in flue gas from the combustion of coke or in any other feasible manner. I may use ammonium carbonate solutions containing any amount of CO_2 up to saturation, but I prefer to use solutions containing a ratio of about 2 parts of CO_2 (grams per liter) and 3 parts of NH_3 (grams per liter); for example, an ammonium carbonate solution containing 40 grams per liter of CO_2 and 60 grams per liter of NH_3 . While it is possible to make use of an aqueous solution of ammonium carbonate such as might be commercially available or produced by dissolving ammonium carbonate in water, I prefer to make my

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solution in the foregoing manner as in this way I have practical control of the NH_3 to CO_2 ratio and it is less expensive. I then add copper to the ammonium carbonate solution and finally add oxygen to form the cupric salt. The copper may be added by contacting the copper metal with the ammonium carbonate solution in a suitable tank or vessel and then bubbling in air or oxygen. Sufficient oxygen should be added to convert all or nearly all the copper which is dissolved by the ammonium carbonate solution to the cupric state. Some cuprous salt can be tolerated but I prefer to use solutions containing as near as practicable 100% of the copper in the cupric state. Various concentrations of cupric ammonium carbonate can be employed but for good yields and a satisfactory product I have found it desirable to use those in which the copper content approaches saturation. To state the desired concentration in another way, it is desirable to employ solutions in which the copper concentration varies from about 50 grams per liter to about 100 grams per liter, CO_2 and NH_3 varying from about 31 to 63 grams per liter in the case of CO_2 and from about 47 to 95 grams per liter in the case of NH_3 . This would represent a mol ratio of Cu to CO_2 of about 1.0 to 0.9 and a mol ratio of Cu to NH_3 of about 1 to 3.5.

In respect to the concentration of the sodium hydroxide solution used as a precipitant, the optimum conditions are indicated in Fig. 1 where it will be seen that satisfactorily low density is attained when the solution of sodium hydroxide runs between 15% and 50% while a very satisfactory concentration is between 20% and 30%. If the concentration is too high it becomes somewhat viscous and accordingly I prefer to operate in the range of 20% to 30%, that is, in about the upper two thirds of the density curve as seen in Fig. 1. In respect to reaction temperature, its very important effect is illustrated in Fig. 2 where the apparent density curve is seen to drop from about 75 to about 35 grams per 100 cc. as the temperature increases from 80° to 140° F. At the same time the yield increases somewhat so that it is quite feasible to take advantage of the lower density resulting from the elevation of temperature.

In Fig. 3 I have shown the results of a study involving the time during which the precipitate is left in contact with the mother liquor. It will be seen that a standing period of from 1 to 8 hours is beneficial both as to yield and lower density while the maximum benefit is achieved where the standing period is from 1½ to 4 hours. By reference to Fig. 4 it will be seen that very material advantages in lower density of product can be obtained by adding the copper solution to the caustic precipitant instead of the reverse. The heavy lines indicate the yield (using a solution containing 49.5 grams per liter of copper, 31 grams per liter of CO_2 and 50 grams per liter of NH_3) and since it is desirable to obtain a yield of 85% to 95%, only the extreme upper ends of the heavy lines can be considered to indicate desirable conditions of operation. Considering the highest point on the heavy line indicating the addition of copper solution to the sodium hydroxide solution, it will be seen that the yield is in the order of 90% which is satisfactory and that at this point the corresponding density is of the order of 32 grams per 100 cc. whereas if the precipitant had been added to the copper solution, the yield would be somewhat below 85%

while the density would be in the order of 50 grams per 100 cc.

Properly prepared solutions of cupric ammonium carbonate mixed with the proper amount of caustic soda under the optimum conditions as above indicated will yield about 1.1 pound of cupric hydroxide for each pound of caustic (76% Na_2O). The amount used is essentially that required to combine with the CO_2 present. The precipitates formed can be filtered from the solution and washed to remove sodium and ammonium salts. They can be readily dried at a moderate temperature lower than would convert any of the hydrate to the oxide. However, if the drying temperature is allowed to go too high some of the hydrate will be converted to the oxide. The temperature best suited for drying is a variable depending on the contained moisture, the density etc. It can be stated generally that the drying temperature should not be allowed to go materially higher than 160°F . and at the beginning of the drying it should preferably be considerably lower than 160°F ., for example, preferably, not above 130°F . As the moisture in the material is driven off by the drying, the cupric hydrate becomes powdery, and when dry is entirely suitable without further grinding for use in chemical processes and for other purposes. Where extremely fine particle size requirements must be met, the powder consisting of agglomerated particles of finer cupric hydrate crystals may be further broken up by grinding in suitable equipment to the ultimate crystal size required.

After the precipitation, the mother liquor will contain sodium carbonate, a small amount of copper, ammonium carbonate and water. It can be treated by heating the solution sufficiently to drive off the ammonia and any CO_2 in excess of that in stoichiometric proportion with the Na_2O content which may be present in the solution. The ammonia and CO_2 gases along with water vapor can be condensed, forming aqueous ammonium carbonate. The residual copper can then be precipitated as a compound such as cupric oxide which can be filtered off. The resulting solution, containing sodium carbonate and water, can be treated by adding calcium hydroxide to reform sodium hydroxide. The resulting calcium carbonate precipitate can be removed and burned to produce CO_2 , which can be absorbed in NH_3 solution, and calcium oxide, which, when slaked, reforms calcium hydroxide. It is seen that all reagents, except copper water and air, entering the process are recoverable in a form such that they may be directly returned after suitable adjustment of concentration to the process.

The following specific example will serve to illustrate the invention:

Example

An ammonium carbonate solution was prepared by adding CO_2 gas to an ammonium hydroxide solution containing 67 grams per liter of NH_3 . The gassing was continued until the solution contained 40 grams per liter of CO_2 . The resulting ammonium carbonate solution was contacted with copper metal and air was blown in until the copper content was 64 grams per liter, an analysis at this point showed 64 grams per liter of copper, 40 grams per liter of CO_2 and 60 grams per liter of NH_3 . A sodium hydroxide solution was prepared containing 252 grams per liter of sodium hydroxide. 264 gallons of the cupric ammonium carbonate solution were added

to 95 gallons of the sodium hydroxide solution at a temperature of 120°F . with violent agitation, the addition being completed in 90 seconds. The precipitate which formed was allowed to stand in contact with the mother liquor for two hours and then was removed by filtration. The precipitate so produced was dried at 120°F . for 10 hours and then at 160°F . for 3 hours until there was no further loss of weight. The product was found to be a cupric hydroxide having an apparent density of 35, that is, a 100 ml. graduate filled to the 100 ml. mark with the material as tightly as would result from tapping the graduate on a table top weighed 35 grams.

Having thus described my invention, what I claim is:

1. A process of producing cupric hydroxide in the form of a finely divided, light fluffy powder of apparent density less than about 65 grams per 100 cc., said process including the steps of (1) preparing an aqueous solution of cupric ammonium carbonate containing from 50 to 100 grams per liter of Cu, 31 to 63 grams per liter of CO_2 , and 47 to 95 grams per liter of NH_3 ; (2) adding said aqueous solution to an aqueous solution of NaOH containing from 15% to 50% NaOH by weight, the quantity of NaOH solution employed being from 80% to 120% of the quantity theoretically required to precipitate all the copper from the cupric ammonium carbonate solution employed, the temperature of the reaction mixture being maintained within the range from 100°F . to 120°F .; and (3) separating the precipitate from the liquid portion of the reaction mixture.

2. A process of producing cupric hydroxide in the form of a finely divided, light fluffy powder of apparent density less than about 65 grams per 100 cc., said process including the steps of (1) preparing an aqueous solution of cupric ammonium carbonate containing from 50 to 100 grams per liter of Cu, 31 to 63 grams per liter of CO_2 , and 47 to 95 grams per liter of NH_3 ; (2) adding said aqueous solution to an aqueous solution of NaOH containing from 15% to 50% NaOH by weight, the quantity of NaOH solution employed being from 80% to 120% of the quantity theoretically required to precipitate all the copper from the cupric ammonium carbonate solution employed, the temperature of the reaction mixture being maintained within the range from 100°F . to 120°F .; (3) allowing the resulting precipitate to stand for a period of from 1 to 8 hours in contact with the liquid portion of the reaction mixture; and (4) separating the precipitate from said liquid portion of the reaction mixture.

PERCY J. ROWE.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,867,357	Furness	July 12, 1932

OTHER REFERENCES

J. W. Mellor's, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," vol. 3, 1923 ed., pp. 143, 144. Longmans, Green and Co., N. Y., publishers.

McPherson and Henderson, "A Course in General Chemistry," 1927 ed., p. 618. Ginn and Co., N. Y., publishers.

UNITED STATES PATENT OFFICE

2,525,242

MANUFACTURE OF CUPRIC HYDRATE

Percy J. Rowe, Hubbell, Mich., assignor to Lake Chemical Company, Calumet, Mich., a corporation of Michigan

Application July 10, 1946, Serial No. 682,465

2 Claims. (Cl. 23—147)

1

This invention relates to methods for preparing cupric hydroxide and has particular reference to processes involving the preparation of a solution containing cupric copper, ammonia and carbon dioxide (herein for convenience called cupric ammonium carbonate) and the precipitation therefrom, by means of an alkali metal hydroxide precipitant, of cupric hydroxide in controlled physical state, especially in the form of a product of low apparent density suitable for fungicide use, the manufacture of copper naphthenate and the like.

I have discovered that by suitably controlling the concentration of the copper in the cupric ammonium carbonate solution, and also suitably controlling certain additional factors, I am able to produce a finely crystalline cupric hydroxide of low apparent density without sacrificing the yield to any extent. That is, I am able to precipitate a suitably high proportion of the copper content of the cupric ammonium carbonate solution in the form of a cupric hydroxide of low apparent density, the material being in the form of very fine crystalline particles and not as a more or less continuous gel, which is the general conception of cupric hydroxide.

This cupric hydroxide is superior to the copper carbonate formerly used as a raw material source of copper in chemical processes for the manufacture of copper compounds because it is as reactive as the finest of copper carbonates, particularly with organic acids, and in all cases is superior in that no foaming due to evolution of CO_2 attends the reactions. It has, therefore, distinct advantages in the chemical process industries.

It has also definite high fungicidal action and relatively low phytotoxicity, and has high value as an insoluble copper fungicide, and because of its basic nature can be used as an adjuvant to other fungicides and insecticides.

Certain specific examples of the effect of controlling such factors are illustrated in the accompanying drawings, wherein Fig. 1 is a diagram showing the effect of varying the concentration of sodium hydroxide precipitant on the yield and apparent density of the product; Fig. 2 is a diagram showing the effect of temperature on the yield and apparent density; Fig. 3 is a diagram showing the effect on the yield and apparent density of the time during which the precipitate is left in the mother liquor; and Fig. 4 is a diagram showing the effect on yield and apparent density of the method of contacting the copper solution with the precipitant and also showing the effect of the amount of precipitant used. In this connection, it is to be

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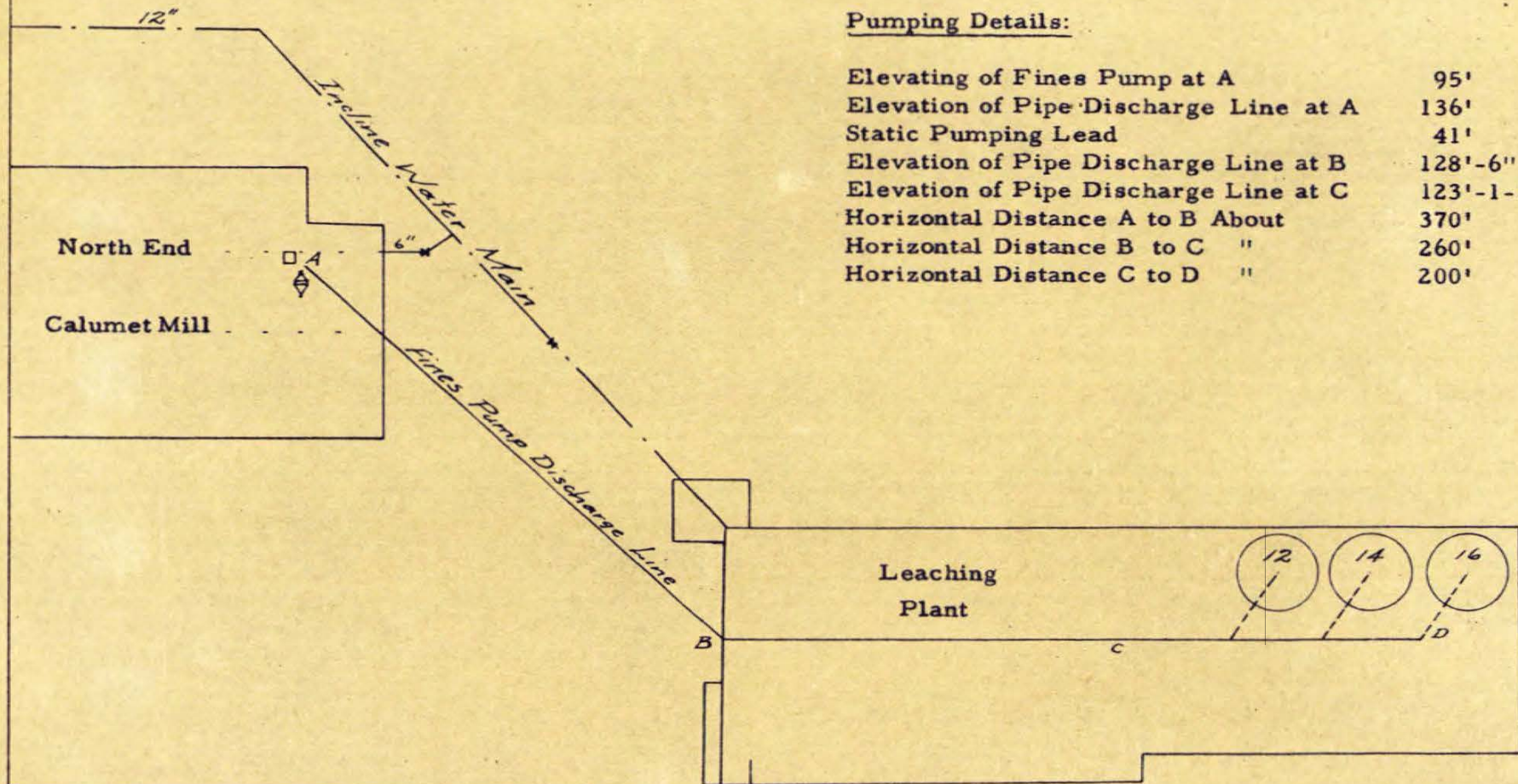
understood that when I refer to apparent density this takes into account the various factors influencing apparent density; such as, fineness and uniformity of particle size and degree of aggregation.

The other factors referred to which are effective at optimum copper concentrations to reduce the apparent density of the product without rendering the yield unsatisfactory are as follows: first, the concentration of the sodium hydroxide (or potassium hydroxide which may be used in equimolecular proportions as a substitute for NaOH) which is used as a precipitant, second, the manner of adding the precipitant, that is, whether the cupric ammonium carbonate is added to the precipitant or vice versa, third, the amount of precipitant solution employed, fourth, the reaction temperature, fifth, the time consumed in completing the mixing of the cupric ammonium carbonate solution with the precipitant, and sixth the length of time the product is left in the mother liquor. I find that it is desirable to select conditions which will result in the precipitation of most but not all of the copper in solution. I regard 95% precipitation as perhaps an optimum but in practice I may operate very satisfactorily on lesser yields, for example 85% to 95%. In order to obtain a high yield, I find it desirable to utilize a copper concentration approaching saturation. This may be varied as will be indicated below. I find it desirable also to maintain in these copper solutions a ratio of essentially two parts of carbon dioxide (grams per liter) to each three parts of NH_3 (grams per liter). This corresponds to a mol ratio of 1 mol of CO_2 to 3.88 mols NH_3 .

Working in the range approximating the optimum concentrations of Cu , CO_2 and NH_3 (which will be defined below), I find that the concentration of the sodium hydroxide solution used as a precipitant has only a slight effect on the yield with respect to copper, but has a more important effect on the apparent density of the product. The sodium hydroxide solution should be fairly concentrated for obtaining the lowest apparent density. It may, for example, vary from about 15% to 50% NaOH on a weight basis and preferably is kept within the range of from 20 to 30%. The quantity of NaOH solution employed may be from 80% to 120% of the quantity theoretically required to precipitate all the copper from the cupric ammonium carbonate solution employed. The reaction temperature has a substantial effect on the yield with respect to copper and a very profound effect upon the density of the resulting product. A desirable temperature range for the reaction is

PLAN VIEW - RECLAMATION OF ALLOUEZ SANDS

487



Pumping Details:

Elevating of Fines Pump at A	95'
Elevation of Pipe Discharge Line at A	136'
Static Pumping Lead	41'
Elevation of Pipe Discharge Line at B	128'-6"
Elevation of Pipe Discharge Line at C	123'-1-1/2"
Horizontal Distance A to B About	370'
Horizontal Distance B to C "	260'
Horizontal Distance C to D "	200'

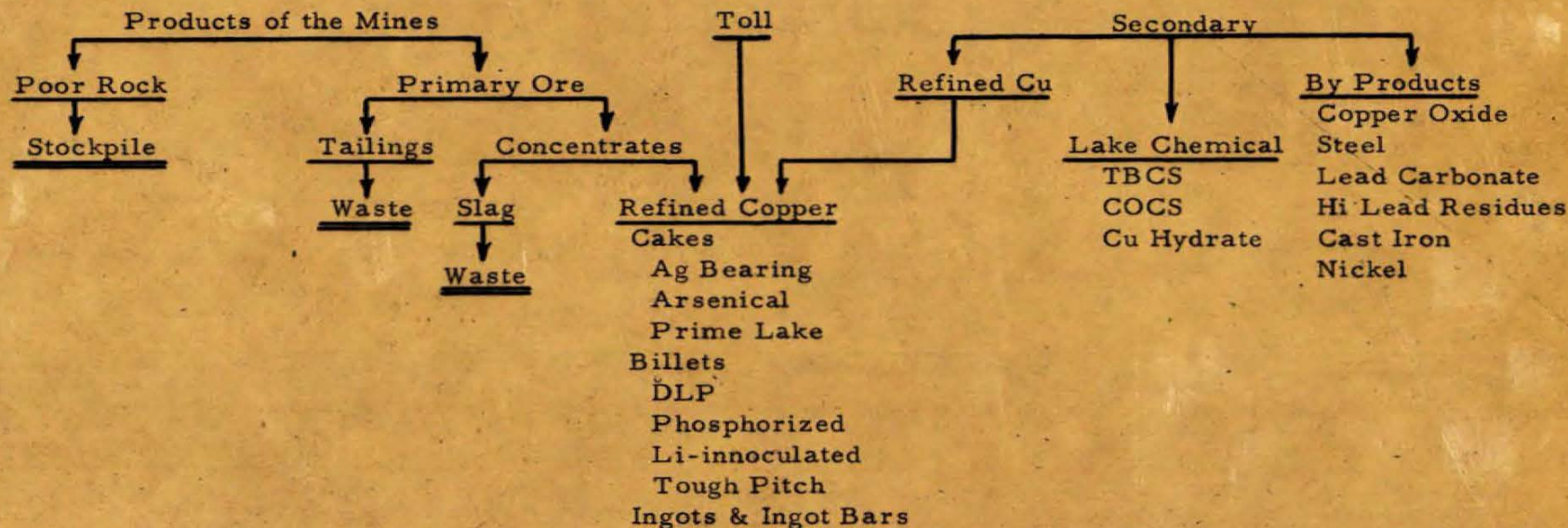
Calumet Division - Calumet & Hecla, Inc.

Research Department

A. B. Landstrom

March 12, 1956

CALUMET DIVISION



Calumet Division - Calumet & Hecla, Inc.
 Research & Development Dept.
 May 1, 1959



Calumet & Hecla, Inc.

CALUMET DIVISION

1 CALUMET AVENUE • CALUMET, MICHIGAN

For Inter-Office Correspondence Only

To Mr. L. F. Engle

Date May 9, 1963

SUBJECT Copper Carbonate

Form 027010

*Reported to
Helen Koman
Marketing 11 AM
5/15/63
by LFB*

We have renewed interest in copper carbonate from Harshaw Chemical Company and our material is being compared with that of Tennessee Corporation. Tennessee's specifications are as follows:

✓ Copper	55.00% Min.	55.26	55.10
✓ Sulphur	.30% Max.	0.43	0.29
✓ Iron	.30% "	0.23	0.20
✓ Zinc	.05% "	0.096	
✓ Nickel	.10% "	0.08	0.06
✓ Lead	.03% "	0.023	
✓ Manganese	.03% "	0.0017	
✓ Chlorides	.005% "	0.035	
✓ Insoluble in HCl	.10% "	0.038	
✓ Arsenic	.001% "	0.0023	
✓ Insoluble in Acetic Acid	.12% "	0.086	
Water soluble salt	1.50% "	0.044	

*From
Sunn
Literature*

They have asked that we supply them with the level of these ingredients in our production.

Please advise when this information will be available.

ACBjr:hek

ACB
A. C. Boorman, Jr.



MS-002
Box 160
Folder 42

*Reported
5-21-63
cp*

5-22-63

MS-002
Box 160
Folder 42

A. C. BOORMAN, JR.

May 22, 1963

Copper Carbonate

This is in reply to your memorandum of May 9, 1963 requesting the analysis of our copper carbonate. Copper, sulphur, iron and nickel was reported verbally to your department on May 15 in order to provide Harshaw with critical analysis promptly.

Copper	55.26
Sulphur	0.43
Iron	0.23
Zinc	0.096
Nickel	0.08
Lead	0.023
Manganese	0.0017
Chlorides	0.035
Insoluble in HCl	0.038
Arsenic	0.0023
Insoluble in Acetic Acid	0.086
Water soluble salt	0.044

May we remind you again that this is the analysis of the product of last season. It is conceivable that minor element contents would vary in the future as additional runs are made. This would be a function of the system's cleanliness and feed material.

May we also advise that the latest literature supplied by Tennessee Corporation for their chemical product shows their analysis of copper carbonate as follows:

COPPER CARBONATE, LIGHT

Cu	55.10
Total S	0.29
H ₂ O Soluble S	0.18
Fe	0.20
Zn	0.03
Ni	0.06
Pb	Nil
Mn	Nil
Insol. in HCl	0.06

LFE/bv
CC; KFF
RVJ

L. F. Engle

MS-002
Box 160
Folder 42

Calumet
& Hecla



CALUMET
DIVISION
CALUMET, MICHIGAN 49913

File: Lake
#1745

For Inter-Office Correspondence Only

To Mr. B. C. Peterson

Date August 24, 1964

Form 022010

SUBJECT Trip Report - August 18, 1964

Niagara Chemical Div. of
Food Machinery Corporation,
Middleport, New York

Persons contacted:

Point of
Contact →

Stewart Bear, President
Tracy Baxter, Purch. Agent
R. R. (Dick) Heinze, Chief Chemist
Mr. Duckworth, Mgr. of Ag Products Div.

Mr. B. C. Peterson and I met with the above-named individuals on Tuesday, August 18, to review our respective positions and interests in Lake Chemical -- Lake Chemical having recently been purchased by Calumet, and Niagara being the chief customer of Lake Chemical. Prior to our purchase of Lake Chemical, Harshaw maintained, for all practical purposes, sole contact with personnel of Niagara.

During the conference several items were discussed as follows:

- 1) Niagara will continue to place orders for C-O-C-S bags. When an order is placed they will send us a copy of the order, and when delivery has been made and when Niagara has been billed for the bags they will send us a copy of the invoice and we, in turn, will issue a credit memo, as in the past.
- 2) They asked that we do all we could to insure availability of cars on rush shipments. Could our Traffic Department make some arrangements with the railroad on having a car or two on the siding available for C-O-C-S shipment, particularly during the peak season?
- 3) Mr. Heinze, Chief Chemist and Quality Control Manager, was called in to discuss specifications and analysis of C-O-C-S. They want us to include Marasperse to the extent of 1% in our formulation, unless we are already doing so. If we are, we are to increase the additive to a total of 1%.

While we were at Middleport they had two complaints relating to lumpy material from the field -- one from the Middleport area and another from the Jacksonville, Florida, area. Mr. Heinze supplied me a sample of material from Jacksonville which contained lumpy material, for examination by our Quality Control and Production groups. Every effort should be made to insure that lumpy material is not present in the bagged product.

For Inter-Office Correspondence Only

To Mr. B. C. Peterson

p. 2

Date August 24, 1964

Form 0220.10

SUBJECT Trip Report - August 18, 1964

Niagara Chemical Div. of
Food Machinery Corporation,
Middleport, New York

- ✓ 4) I gave them a copy of Lake Chemical specifications for C-O-C-S dated January 1, 1964, for their examination and review. Mr. Heinze asked specifically if the specifications and test procedures dated 2/25/52 and revised 6/22/53 were being complied with. A copy of these specifications and test procedures is attached.
- ✓ 5) Provision is made on the C-O-C-S bag for a batch number on the lower right-hand face of the C-O-C-S bag. They have asked that we devise a coding system to indicate the production or lot number so that the lot number, etc. appears on the bag. From this, of course, details of the production could be traced on any complaints received. Further, Mr. Heinze asked that we forward to Niagara a 1# composite sample of our daily production of C-O-C-S, appropriately marked with batch number, etc.
- 6) We were cautioned again to be sure not to send any of our invoices to the end-user or to Niagara's customers. This has happened in the past, but very infrequently.

During the course of our visit we had an opportunity to tour their R&D facilities. I was tremendously impressed with the nature of the work undertaken in the area of pesticides. Over a 2-year period they have spent approximately \$2,000,000 for their research building and equipment. They employ in this facility approximately 115 men, including about 50 PhD's. They screen approximately 2500 organic chemicals a year for biological activity, and have as a target the development of one chemical for commercial production and sale, as a result of this work, each year.

ACBjr:hek

A. C. Boorman, Jr.

LAKE CHEMICAL COMPANY
Calumet, Michigan

SPECIFICATIONS

PRODUCT: Copper Oxychloride Sulphate (C-O-C-S)

DESCRIPTION:

Copper Oxychloride Sulphate, a light blue free flowing powder corresponding to the formula $X(\text{CuCl}_2) \cdot y \text{CuSO}_4 \cdot 5 \text{Cu}(\text{OH})_2$.

MANUFACTURING METHOD:

Reacting metallic copper with sulphuric acid, common salt (NaCl) and air. Control of pH with ammonia and sulphuric acid. Fine solution pH 7.3 - 7.4. Product designed to carry 9.0 - 10.0% Cl and 6.0 - 7.0% SO_4 .

CHEMICAL PROPERTIES:

Soluble in acids and ammonia
Insoluble in water
Copper 56.0% Min.

PHYSICAL PROPERTIES:

S. G.	3.3
Pounds per gallon	27.49
Bulking Value	0.0364 gallons per pound
Bulk Density	30 - 35 lbs./cu. ft.
Average Particle Size	2.5 microns

TYPICAL USES:

As a spray for the control of foliar diseases and as a component of dust and spray formulations. Not recommended for use as a dust in concentrated form (55%).

MANUFACTURING AND USE HAZARDS:

Poison - corrective measures shown on label.

Date: 1-1-64

Original Date: 2/25/52
Revised: 6/22/53

June 22, 1953

SPECIFICATIONS FOR PURCHASED MATERIAL:

Trade or Common Name:	C-O-C-S
Chemical Name:	Copper Oxychloride Sulphate
Manufacturer:	Lake Chemical Company
Code No:	557

PHYSICAL SPECIFICATIONS:

Physical State	Fine, free-flowing powder
Bulk Density (Vol. in cc of 27.7 g. in 100 cc cylinder)	80-100 cu. in.
Color	Celestial blue
Odor	None
Screen Analysis - Wet through 325	99-1/2% Min. (Note 1)
Solubility of active ingred- ient in water	.0006 - .0001 lbs/100 gal (Note 2)
pH at dilution used	7.5 to 8.5 (Note 3)
Dispersibility	97% Min. (Note 4)

CHEMICAL SPECIFICATIONS:

Assay	56.5% Met. Cu. Min. (Dry Basis)
Other ingredients	(chlorides 9.0-10.0 (sulphates 6.0-7.0%)
Moisture	2% Max. (4 hrs. @ 105°C)
Method of Assay	Conventional Hypo titration
Methods of Analysis	Methods for chlorides & sulphates to be supplied by Harshaw

Authority: Letter from W. W. Harris, Harshaw Chemical Co., to
J. F. LesVeaux, dated February 21, 1952. Revised authority: per
Letter W. W. Harris to C. O. Eddy dated June 12, 1953

(All signatures were not legible)

(Signed) John F. LesVeaux
J. F. LesVeaux

(Signed) J. R. Warren
" J. R. Jones
" C. A. McDonald
" F. S. Black

JRW/mb

cc: JVV-SHB-EKH-VGA-FKC-EDB-MLT-JRJ-CAM-JHH-HWD-JFL-FSB-HW-EPB-CC
CCC-JLP-OC-CMT-JRW-JF-DADE-ALLEN-DUCKWORTH-ALDEN-WILLAN

Note 1 - Wet 325-m screen test.

10 g. sample is stirred into 300 cc tap water, thoroughly dispersed, poured through grease-free 325-m screen, washed through with running tap water using soft brush to break up aggregates. Residue is filtered in tared gooch filter and weighed.

Note 2 - 4.8 grams COCS is soaked in 1 L. distilled water with occasional shaking for 24 hrs. Filtered, 500 cc aliquot taken, 1 cc conc. sulphuric acid added and evaporated to fumes of H_2SO_4 . If residue is discolored, add few drops of HNO_3 and digest to clear residue. Dilute to about 20 cc, make strongly alkaline with NH_4OH , filter into Nessler tube (slight iron ppt may be filtered out, make to 100 cc and compare with standard copper solution treated in same manner.

Note 3 - 6 g. COCS is thoroughly soaked in 1 L. water for 5 minutes with shaking. Aliquot is taken and pH determined with glass electrode.

Note 4 - 15 g. COCS is put into 2500 ml tap water and allowed to wet, stirred for 1 minute and poured through a clean 325-m screen, washing with slow-running tap water without brushing or other mechanical disturbance. Residue is washed into tared gooch, dried and weighed.

MS-002
Box 160
Folder 42

file 1745
NED
LFE
September 18, 1964

Mr. Tracy Baxter
Niagara Chemical Div.
FMC Corporation
Middleport, New York



Dear Tracy:

We have now completed a review of the several points discussed in our August meeting and restated in your letter of August 19.

Item I - Marasperse

Marasperse has not been added to C-O-C-S. The consensus here is that our equipment layout is not conducive to accurate additions of this ingredient. System modification costs would be in excess of \$20,000 to accommodate Marasperse. Figures 1 and 2 are attached, showing a) the current layout, and b) that layout which would be necessary if Marasperse were added. Probably a more important consideration than costs is that a 1% addition would reduce our copper content by approximately that amount and it would be difficult, if not impossible, to maintain a 56% copper analysis.

Lumpy material occurs infrequently and present control is good. Damp material from the dryer or a damaged pulverizer screen is the cause. The former occurs when we attempt to push the equipment beyond its capacity. A damaged screen is detected immediately by sound and is replaced as necessary. The bag, and the preceding bag which was being loaded when damage occurs, is dumped back into the circuit and rerun. We will endeavor to achieve additional drying at the filter. We now use a bank of heat lamps but we could possibly arrange for air circulation in this area to get additional evaporation.

Item II - Test Methods

We do not analyze for the physical specs other than dispersibility, however we do run all the chemical tests. Methods of analysis differ in some cases.

The sampling procedure consists of a spoonful from every fifth bag. There are forty 50# bags to a pallet and 3 pallets or 6,000# to a lot. Copper is determined on each lot by the attached method, which differs from the method given in the specification, and gives more accurate but slightly higher results. The % copper is reported on an as-is basis and our spec calls for 56.5% Cu min.

on a dry basis. Therefore, the past figures should be divided by 100 minus %H₂O to give the actual copper percentage on a dry basis.

The standard deviation (σ) for 38 composite samples of carload lots shipped between 3-8-61 and 3-27-64 was determined. Values are given in Table I. Also shown in Table I are the values at $\pm 1\sigma$, $\pm 2\sigma$, and $\pm 3\sigma$, or $\pm 15.86\%$, $\pm 2.28\%$ and $\pm 0.135\%$. This means that with copper for example, the value at -3σ is 56.58% and only 0.135% of 38 carloads would be expected to fall below 56.58% copper.

Copper

We definitely meet the specification using our attached method of analysis. With the iodimetric titration method which gives low results, some material may be slightly less than the specification of 56.5%. The statistical difference between the two methods of analysis could be determined if required.

Chloride

Although the average % Cl is 9.45, about 30% of the material falls outside the specification range of 9 to 10. A more realistic range would be 8 to 11. Our method of analysis for chloride in C-O-C-S differs from the method specified. We run a gravimetric chloride determination with silver chloride, whereas the Harshaw method is a titration with mercuric nitrate. The gravimetric method should be more accurate.

Sulfate

The average is 6.18% with again about 30% of production outside the range of 6 - 7. More realistic range would be 5 - 8. Our method of analysis is basically the same as called for but with short-cuts, which could be responsible for some of the spread shown in the sulfate values.

%H₂O

We consistently are below 1.9% H₂O and the specification calls for 2.0% maximum. Method is same as specified.

Dispersibility

The specification calls for 97% minimum. Only 0.135% of our production is below 98.1. This is a very good test to pick up lumpy material and its use could be expanded if necessary for control purposes. Method of analysis is the same as given in the spec.

Mr. Tracy Baxter, p. 3

September 18, 1964

In general, our product is well within specification. It would appear that if the deviation in chloride and sulfate content was critical we would have had complaints on performance in the past.

Item III - Lot numbers

Lot numbers will be stamped on each bag, starting with the next shipment, since we do have our current inventory recorded by lot number. Future production will, likewise, show lot numbers.

Item IV - Samples

A 1# sample of each day's production will be marked with the appropriate lot numbers and will be forwarded to Mr. Heinze for analysis.

We expect to start production the week of September 21 for the coming season. After we are under way, I would encourage a visit by Mr. Heinze in Calumet. He could then observe our operation and talk about it with our Production, Quality Control, and Development personnel.

Very truly yours,

CALUMET DIVISION
Calumet & Hecla, Inc.

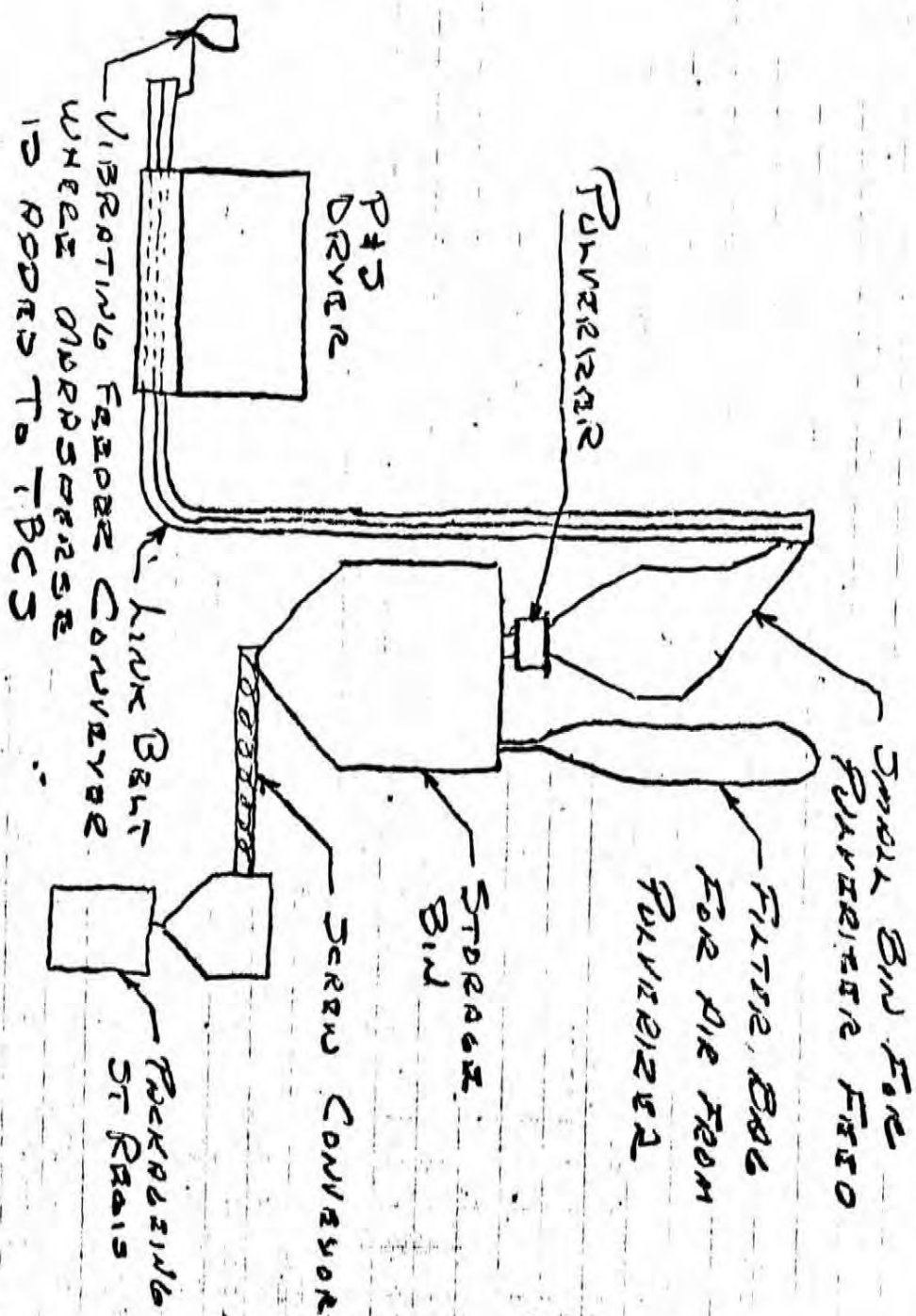
ACB

A. C. Boorman, Jr.
Director of Marketing

ACBjr:hek

encs

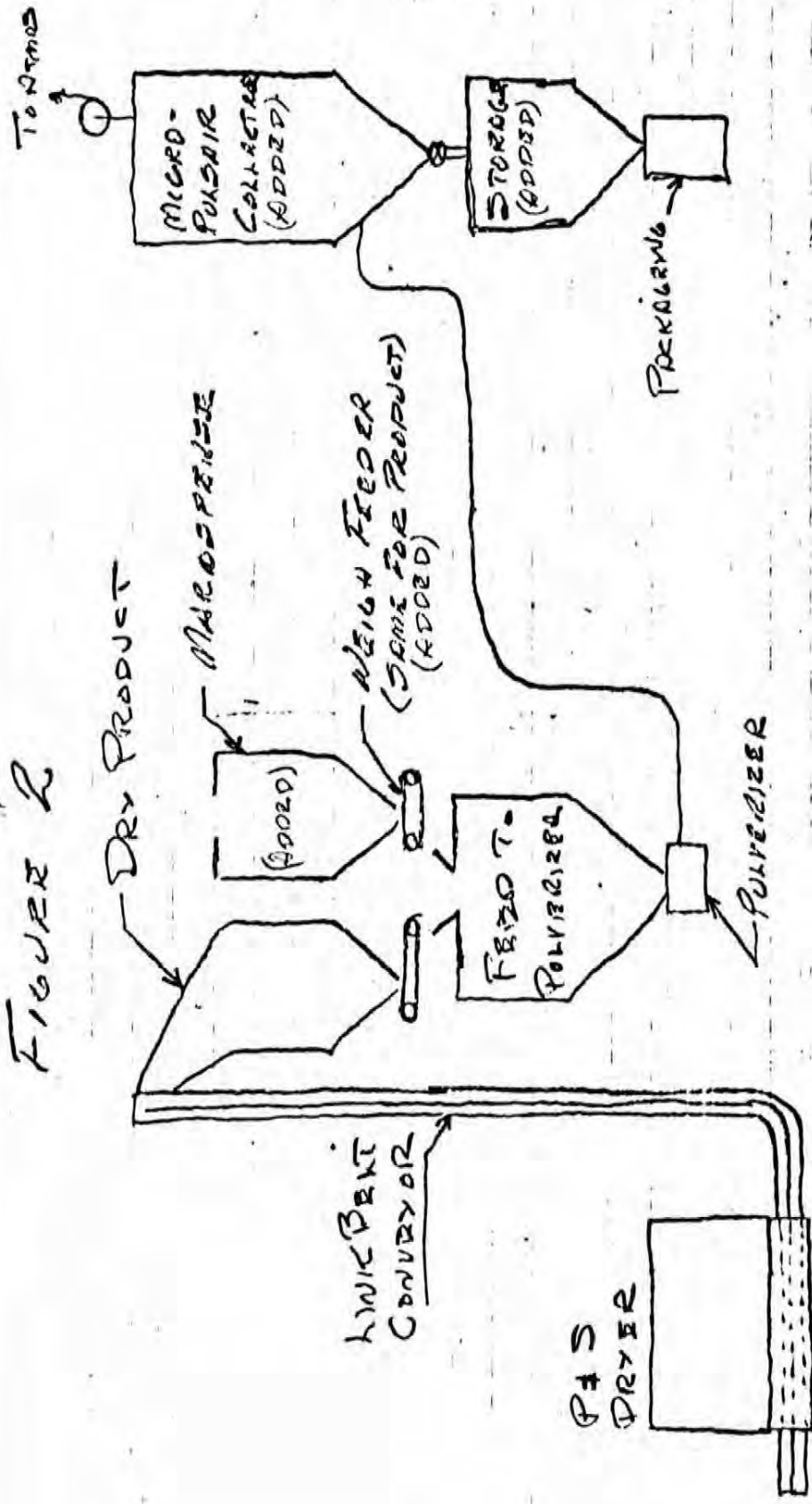
FIGURE 1



DRY PRODUCT HANDLING SYSTEM
 Dry Product Handling - Large Capacity

8/20/64 H. H. H.

FIGURE 2



POWDER ALIGNMENT OF EQUIPMENT

FOR DRY PRODUCT HANDLING - LARRE CHEMICAL

ADDITIONAL EQUIPMENT

- 1 STORAGE BIN FOR PRODUCT
- 1 " " " " " " " "
- 2 WEIGH FEEDERS
- 1 MICRO PULSAR COLLECTOR.

2/27/64 Kby

TABLE I

ANALYSIS OF C-O-C-S SHIPMENTS 3/61-8/61

501

TEST	SPECIFICATION	AVERAGE 38 CARBONS	STANDARD DEVIATION	-3 σ 0.135%	-2 σ 2.28%	- σ 15.86%	+ σ 15.86%	+2 σ 2.28%	+3 σ 0.135%
% Cu	56.5% MIN.	57.34	0.752	56.58	56.84	57.09	57.59	57.84	58.10
% Q	9-10	9.45	0.516	7.90	8.42	8.93	9.97	10.48	11.00
% SO ₄	6-7	6.18	0.533	4.58	5.11	5.65	6.71	7.25	7.78
% H ₂ O	2.0% MAX.	1.70	0.06	1.51	1.57	1.64	1.76	1.83	1.89
% DISPER.	97.0% MIN.	98.99	0.305	98.1	98.4	98.7	99.3	99.6	99.9

8/28/64 eddy

CALUMET & HECLA, INC.
Calumet Division

ANALYTICAL PROCEDURE FOR % COPPER IN C-O-C-S

Weigh 2 g / C-O-C-S into 300 ml tall form beaker.

Add approximately 25 cc distilled water.

Add 35 cc stock solution #1.

Heat until dissolved and dilute to approximately 150 cc.

Plate out copper on platinum electrode at 0.25 amps. for approximately 18 hours.

Check solution for remaining copper by adding 1 drop to a spot plate containing 1 drop of H_2S solution. Brown color indicates presence of copper and plating must be continued until no brown color is observed.

Weigh electrode after washing and drying.

$$\frac{(\text{Wt. electrode / copper}) - \text{wt. electrode}}{\text{Wt. sample}} \times 100 = \% \text{ copper}$$

Stock solution #1

2500 ml distilled H_2O
800 ml conc. HNO_3
800 ml conc. H_2SO_4

DATE: February 18, 1966

TO: Dr. C. P. Stanford

cc: Messrs. R. W. Johnson
R. R. Allen

Calumet
& Hecla

EXECUTIVE OFFICES

MS-002
Box 558
Folder 12

SUBJECT: Some Considerations for our Future in the Agricultural and Industrial Chemicals Business

Review

In addition to our supplying of copper oxides, carbonates, and hydrates to the industrial complexes involved in marine paints, ceramics, Petro-Chemical catalysts, and other applications; we are furnishing the agricultural trade with copper oxides for trace mineral additives in fertilizer and animal feeds, and furnishing other copper chemical (tri basic copper sulfate, copper oxychloride sulfate, neutral copper dust base) for fungicide.

Present developments involve the possibilities of our production of Cuprous oxide for marine paints; a copper dithiocarbonate fungicide; a "water" soluble copper concentrate for "immediate need" sprays; and a copper algicide.

Limitations of our Present Product and Marketing

1. Few of our chemicals are in the form of final use
 - a) industrials require further process before end use
 - b) agriculturals require a dispersment media for fertilizer and feeds and require a mixture formula of other products (sulfur-DDT etc.) prior to fungicidal use.
2. Distance from our raw materials source
3. Distance from our markets
4. Little marketing follow-up to testing programs
5. Dependency on very few customers for the total volume
6. The specific end market is unknown (who, why, what price)

7. Location of the sales office at Calumet handicaps travel
8. Ineffectual and incomplete advertising brochures and media distribution
9. Lack of product "Glamour"
10. Lack of essentially related products

Program for Improvement in Product and Marketing

In preparation for a more encompassing line of products ~~leading~~ eventually to a "Chemicals" Division of Calumet & Hecla, Inc. we might:

1. Establish a Chemical Marketing Section in Chicago, perhaps housing at the corporate office with complete marketing autonomy.
 - a) Assume control of all Chemical Marketing
 - b) Remain under the Calumet Divisional command
2. Create a broader market base for our chemicals by
 - a) Determining the end user, his use demands, and the competitive situation
 - 1) Reply card contest in our agricultural product bags
 - 2) Assign a man to work closely with Traylor Chemical to determine his market and operational advantage
 - b) Soliciting the large fertilizer manufacturers, coops, area "mixers," and animal feed producer
 - 1) Determine potentials for copper and related trace minerals
 - 2) Create a mailing list and establish the credit responsibility

- c) Expand our industrial market
- 3. Create a "Glamour" image for our products
 - a) Redesign bags and rename the products
 - b) Revise all brochures for appearance, name, and completeness of technical information and usage recommendations
- 4. Ascertain possible related products and extensions of our present line during marketing solicitations
- 5. Ascertain the prospects of a complete and ready mixed product
- 6. Inaugurate a detailed freight cost study of the product to market
 - a) Possible gimmick on advantages^{of} shipping form
 - b) Prospects of "2 way" freight ~~in~~ ^{mail}s
 - c) Contract carriers
- 7. Coordinate marketing and testing programs to assure follow-up of and product availability to new areas of tests
- 8. Examine the prospects for total trace mineral mixes based on purchased materials
 - a) Test market the "full" mix
 - 1) Form a contest on a package "Test Plot" success trial
 - 2) Grass roots promotion in the test are with mixer and/or coop
 - b) If successful determine feasibility and priority for becoming basic in the additional trace minerals
- 9. Plan a research program toward the goals desired

10. Begin an analysis of the raw material source points for all materials ultimately desired

- a) Freight considerators
- b) Availability considerators

11. Detail a search into the necessary equipment to accomplish the planned goal

- a) Costs (capacities-expansion needs)
- b) Productivity desired
- c) Physical facility and location

12. Chemicals Division Creation

The assignment of all chemical sales to a new office would allow the development of the prospective Chemical Division to proceed toward reality and at the same time improve our current profitability and market vulnerability.

S. N. Hartwell
S. N. Hartwell

ylw

Copy to Chem Jels
to Les Engle

COPPER OXIDE vs COPPER SULFATE

1. Dr. Harry W Titus: "Copper sulfate, or bluestone, was the first copper compound to be added to commercial mixed feeds. In the past few years, however, it has been, and is being, replaced by copper hydroxide and copper oxide." -- 9 April 1956, Terre Haute, Indiana.
 2. Dr Harry W Titus: "Compounds of iron, manganese, copper and cobalt that are soluble in water are not suitable for use in mixed feeds because the ions of these four elements catalyze the oxidative destruction of the fat-soluble vitamins, A,D and E." 9 April 1956.
 3. Allen T Ralston: "Copper oxide is recommended where supplementation of copper is necessary." -- Washington Beef Cattle Day 1960.
 4. Drs Buescher, Griffin and Bell: "There was a greater amount of copper carbonate excreted via the urine than of copper oxide or copper sulfate. The availabilities of the three forms of inorganic copper compounds for swine were similar." -- Journal of Animal Science Vol. 20, No. 3, August 1961.
 5. Dr H D Ritchie: "The use of copper sulfate in these trials gave poorer performance than copper oxide, possibly indicating toxicity." -- Journal of Animal Science, 21, 4, 1010.
 6. Dr R J Bunch: "Copper oxide fed at the same level (250 ppm) also improved gains and feed efficiency to nearly the same extent. Because of the hemoglobin interference using the sulfate, it may prove preferable to use the oxide." -- FEED AGE, January 1961.
 7. Drs Bunch, Speer, Hays, Hawbaker and Caton: "The feeding of copper oxide resulted in small increases in copper content of the tissues, whereas the feeding of copper sulfate resulted in marked increases in tissue copper content." -- Journal of Animal Science, November 1961.
 8. John W Megown: "The water-insoluble compound, copper oxide, is the preferred source of nutritional copper." --Western Feed, June 1964.
 9. Dr. Virgil W Hays: "Feed manufacturers and researchers in Great Britain have accepted 200 to 250 ppm of Cu from copper sulfate or copper oxide as a routine feed additive and are successfully using it in their swine rations." FEEDSTUFFS, April 14, 1964.
- AND--in comparing costs, it is well to remember that 1 pound of BROWN COPP 75 supplies the same amount of copper as 3 pounds of copper sulfate -- currently selling at about 20¢ per pound.

MAY 1966

ms-002

Box 558

Folder 12



1916

H. E. Day
cc: LGS ✓
LRJ
Reading File # 2

January 22, 1968

The screen sizings and chemical analysis of various C & H products that you requested are as follows:

	<u>SCREEN SIZING</u>	
	<u>1-325 Mesh.</u>	<u>1-200 Mesh.</u>
Fertilizer "50"	90.4	95.2
Fertilizer "75"	98.4	99.2
Feed "75"	97.6	----
H1 Cu ₂ O with chippings	97.6	----
H1 Cu ₂ O without chippings	98.8	----
H1 CuO with chippings	93.6	----
H1 CuO without chippings	Sample not available this month.	
N.C.D.B. "83"	98.8	----
# 1 Cupric	98.8	----

CUPRIC OXIDE (BLACK)

0.027% PBO₂

0.050% Fe

N.C.D.B. -83

Solubility 72 hours at pH 1.0 using HCL.

Total Cu-----83.17%

Cu dissolved-----30.90%

MS-002
Box 164
Folder 2

COPPER HYDRATE

Composite sample covering one month production.

Total Cu-----	63.590%
OH-----	33.750%
Na-----	0.230%
NH ₃ -----	0.084%
CO ₂ -----	0.190%
SO ₄ -----	0.250%
NO ₃ -----	Nil
CL-----	0.020%
HNO ₃ insoluble-----	0.006%
Ca as Ca & Mg-----	0.016%
Fe-----	0.013%
H ₂ O-----	1.200%

"B" CIRCUIT COPPER OXIDE

Cu ₂ O-----	65.27%	Cu-----	78.53%
CuO-----	25.22%		
Met. Cu-----	0.41%		
Insol in HNO ₃ -----	Nil		
CO ₂ -----	1.93%		
ZNO-----	3.66%		
PBO-----	0.14%		
NiO-----	0.13%		
Fe ₂ O ₃ -----	0.14%		
NH ₃ -----	0.61%		
Moisture-----	0.90%		
Chlorides-----	<u>0.30%</u>		
Bal Na, K, O ₂	98.71%		

1976
Page 3
H. E. Day
January 22, 1968

In addition spectrographic analysis indicates Ag_2O , CaO , MgO , MnO , NiO , SnO_2 , Na_2O and Li_2O in trace amounts less than 0.01%.

MOISTURE COCS

	<u>Date</u>	<u>% H₂O</u>
Lot 370	1-3-68	3.6
Lot 371	1-4-68	3.6
Lot 372	1-5-68	4.0

C. J. Bastian

CJB:amp

MS-002

Box 164

Folder 2



CALUMET

FORM 50043

DIVISION

RESEARCH PROJECT PROGRESS REPORT

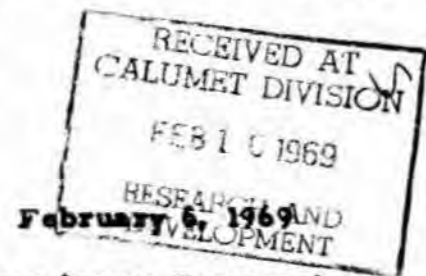
PROJECT NO.
27-20-6
REPORTING PERIOD
1st Qtr. 1968

PROJECT TITLE			
Chemical Processing - CD-1916			
TECHNICAL OBJECTIVE			
Process improvement to reduce costs and improve product quality.			
PROJECT LEADER			
L. C. Klein			
PROJECT * COMPLETE	AMOUNT AUTHORIZED	% EXPENDED	REPORT AUTHORIZED BY
Continuing	\$19,728	15	L. G. Stevens
PROGRESS ACHIEVED			
<p>Slight changes were made at the Tamarack Leaching Plant to adapt the equipment to the production of Cal-Cop-10. Approximately 15,000 gallons of material was produced during the last week in March. Time required for production of the material has been reduced to less than one quarter the time required to produce the material at the Lake Linden Plant, and ammonia losses have been reduced considerably. Additional savings will be made in packaging and handling the material at the Tamarack Plant.</p> <p>Because of the work in disposing of the barium carbonate precipitate from the Lake Linden Leaching lead removal circuit--about six barrels a day--the possibility of reducing the amount of residue was investigated. Instead of filtering all of the precipitate formed, somewhat more than half of it has been re-introduced into the system to determine whether it would collect more lead, and the amount of barium chloride used to form this precipitate has been reduced from 500 to 250 pounds per day. It has been found that this practice is working satisfactorily with no loss in lead removing efficiency. The amount of precipitate taken from the process has been reduced to two barrels per day, and a saving of \$21.00 per day is being realized from reduced reagent consumption, plus the labor saving in mixing reagents and handling the sludge. The possibility of selling this sludge, which contains about 10% lead, up to 5% tin, copper, and barium carbonate is being investigated.</p> <p>Preliminary equipment layouts, building design, equipment lists, and inventory lists for a new chemical and leaching plant were developed during the quarter, and will be reported on during the first half of April.</p> <p>A process for making COCS which derives most of its copper content from copper oxides was developed in the lab and a full scale run was made at Tamarack. The balance of the copper content in the product comes from scrap copper. The product was satisfactory, and the process is simple and straightforward. The copper oxide used was #1 Cupric but still chippings can also be used.</p>			
ACTION PLANNED NEXT PERIOD			
Additional work on new chemical and leaching facility.			
Technical service on manufacture and packaging of Cal-Cop-10 and as required for other chemical operations.			
Complete testing of process for making COCS to thoroughly evaluate it in order to prepare a production procedure.			

MS-002
Box 164
Folder 5

File
1922

2075
HED



E. Sanderson

: Break-even sales on Tamarack
Leaching Products

In order to determine break-even sales on product lines, certain facts and assumptions must be made. The basis for the break-even sales on Tamarack Leaching products is the 1969 profit plan production, cost, sales data and profit targets. In addition, labor was treated as a period expense.

The break-even sales pounds were predicated upon the above statements and are as follows:

<u>Product Line</u>	<u>Break-even Sales Pounds</u>
Hydrate	126,208
C.O.C.S.	430,450
T.B.C.S.	112,539
Cal-Cop 10	15,622
	<u>684,819</u>

G. E. Lengyel
G. E. Lengyel

GEL:gb
cc: CHS
GLC
LGS ✓
File (2)