Re Denver Flotation Equipme

Doc:

We are particularly anxious to know what the effect of the increased height of liquid in a larger unit will do. Is ther still time, therefore, to change t order to the #7 Denver Sub A Flotation cell which appears to have a volume at least three times that of the unit now being sent to us?

Harry Gold
Joseph E. B. Bower

Data for Table of Results (runs nos 4, 5, 6+7)

	1	4	5	6	7	7(a)
[illegible] / hr	10.7	12.0	12.6	13.2	19.8	18.0
Rate [illegible]	780	1340	1550	1550	1560	1564
→ [illegible] gas	12.2	11.6	12.1	12.0	11.8	7.9
[illegible]	10.9	6.6	5.6	4.7	8.0	5.8
[illegible] eff	11	43	54	61	32	33
[illegible] cov / [illegible] / hr	0.013	0.090	0.135	0.177	0.110	0.070
[illegible] cov / [illegible] / h	0.012	0.084	0.121	no values figured as they would be meaningless.		
[illegible] cov / [illegible] / 24 hrs	400	3000	4400			

[illegible] 67

1. Urgency created   1790 [illegible]
1390 better
1990 [illegible] (one [illegible] recommended)

2. Ave Rate unit need 1.9/4.6

1.5 – 1.8   5.0% increase →
{ current [illegible] .3
Cities 7.0%
& remaining [illegible] way

3. ~~[illegible]~~ capacity of abs.
400 mi to 1,000 mi (11% increase)
practically connect the coal/[illegible] / [illegible]
→ 4 [illegible] and available 1970

Run # 2	[illegible] unit	Tower	rec.
average inlet			
average exit			
lbs. CO2 abs. / hr.			
lbs CO2 / gal soln.		—	—
apparent absn efficiency.		—	—
rate of gas flow. ft³ / gal soln / hr.		0.5	1.0

⑦

$$\frac{49.3 - 32.2}{17.1} \rightarrow 34.6\% \rightarrow 9.0 \text{ gm Na}$$

$$\frac{49.3 - 26.2}{23.1} \longrightarrow 46.8\% = 11.4 \text{ gm Na}$$

$$2.4 \times 0.415 \rightarrow 1.00 \text{ gm CO}_2$$

$$\frac{1.00 \text{ gm CO}_2}{1} \Big| \frac{9000}{100} \Big| \frac{\text{gm cotolal}}{454} \Big| \frac{8.5}{} = 1.69$$

$$\frac{1.69}{0.84 \times 30} \times 100 = 6.7$$

$$\updownarrow$$

$$\frac{11.4}{7.0} \qquad 7.4$$

6.8
1.7
0.6
0.4
1.2
0.9
0.8

12.2
1.7

6/3/44

Program

Finish analytical methods for Furnace Leachings – June 2

---

2 meanwhile, get ready for run on decomposition of NaHCO3 slurry, to determine:

a - rate of evolution of CO_2,

b - steam used,

make run – June 2

---

3 Begin work on separation of salt from Furnace Leachings after preliminary tests, try out at least one scheme – July 1

Leached + Cr –

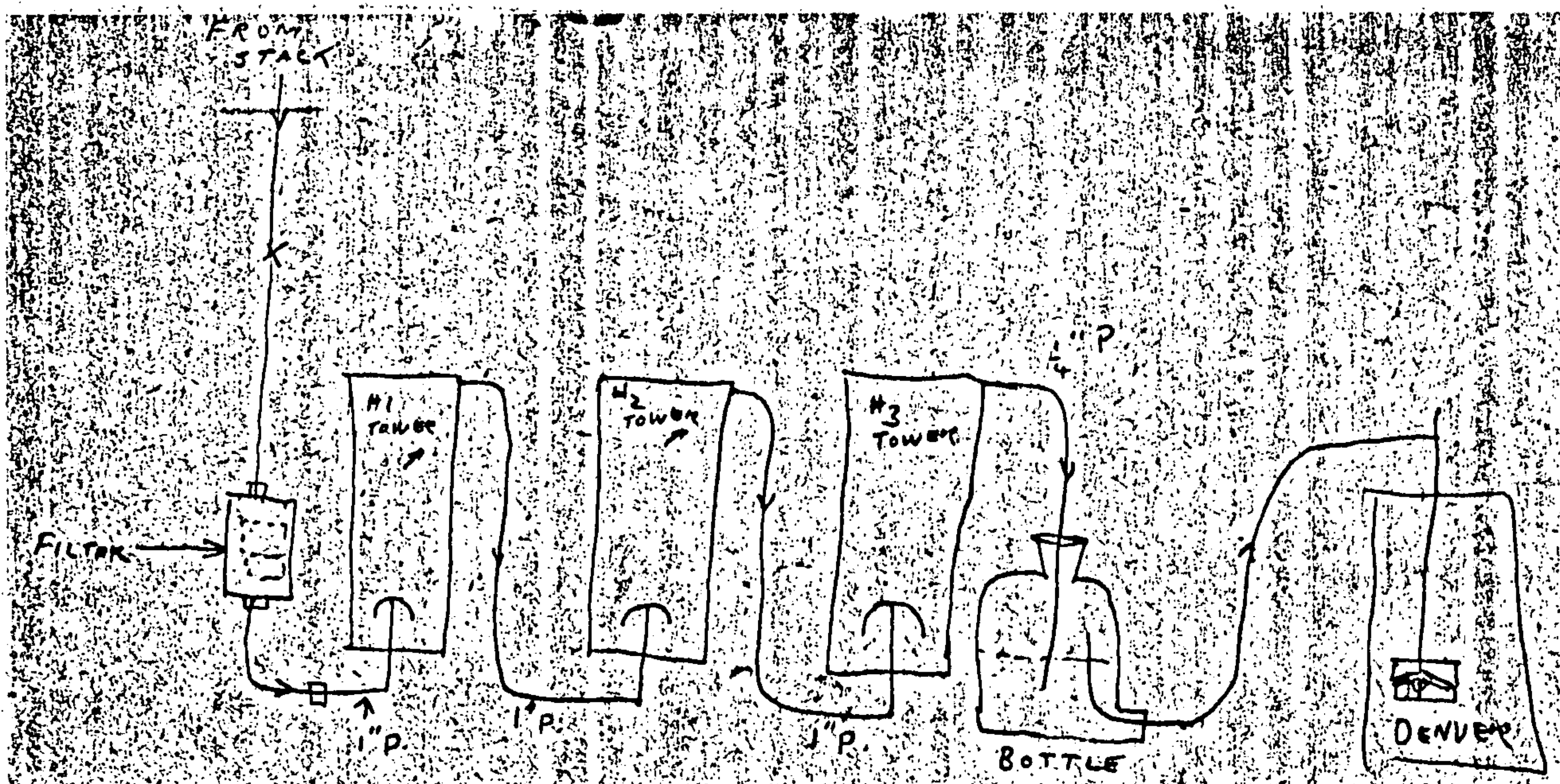
Navy 2

Program

1. Try absorption on larger scale unit to determine:
   a. Power cost
   b. method of operation
   c. Efficiency in removing SO_2.

2. Measure steam necessary for decomposition. This can be done on a 2 or 3 gal. scale.

3. Study removal of SO_2 and dust


FROM STACK
FILTER
#1 TOWER
1"P.
#2 TOWER
1"P.
#3 TOWER
1"P.
1/4"P
BOTTLE
DENVER

5/29/41

Doc:

The Denver equipment is drawing flue gas through three towers and into the absorber proper; there is apparently no decrease in the rate of flow.

Run 16

Data Sample No.	Time	Gas Rate, cfm	Speed, rpm	Gas Analyses, % SO₂: Inlet	Gas Analyses: Exit (corrected)	Gas Analyses: Corrected inlet	Temp, °C	Titration, ml of N-[illegible]: Solution O.C.	Solution M.O.	Total O.C.	Total M.O.
1	10:10 10:40	0.80 0.80 0.80	2190	10.8 10.8 10.8	2.4 2.0 2.4		48	24.8	49.6		
2	10:45 11:16	0.85 0.85 0.85	2200	11.4 10.8	3.6 3.2 [illegible]		48	22.2	49.3		
3	11:25 11:55	0.80 0.80 0.86	2200	8.0 11.2	3.4 3.6 4.0		50	20.1	49.2		
4 ①	[illegible]	0.85 0.85 0.85	2200	11.6 11.6	4.8 5.4 5.2		49	18.1	48.6		
5			2790	X				16.3	48.7		
6 ②	11:55 12:15	0.85 0.85 0.80	2190	11.8 12.6	4.0 4.4 4.4		49	17.3	46.8	16.9	4.92
6 (a)								15.6	43.5	15.1	4.9
7 ③	2:55 3:25	0.90 0.80 0.80 0.75	2260 2250 2230	12.0 11.6 11.4	4.0 3.6 3.6 3.8		50	16.8	45.0	16.6	4.93
7 (a)								15.0	42.5	14.6	4.93

Notes:

① Pre[illegible] at [illegible]

② Added 1 liter of Na₂SO₃ soln. Total vol = 9 liters

③ 1 liter out, Added 1 liter Na₂SO₃ soln.

RUN #5

Data Sample No.	Time	Gas Rate, c.f.p.m.	Speed, r.p.m.	Gas Analyses, % CO₂			Temp., °C	Titration, ml. of N H₂SO₄			
				Inlet	Exit (Outlet)	Corrected		Solution		Total	
								O.C.	M.O.	O.C.	M.O.
1	10:35 to 11:05	0.80 0.80 0.82	2210	11.2	0.4 1.0 1.8		47	24.2	48.7		
2	11:15 to 11:45		2190	14.2 10.6 0.5 10.8	—		49	22.8	47.3		
3	1:35 ② to 2:05	0.80 0.70	2240	11.4 11.2	3.4 4.4 3.6		48	22.6	47.6		
4	2:15 to 2:45	0.85 0.87 0.87	2240	12.2 12.0	3.8 3.8 3.9		49	21.0	47.7		
5	2:55 to 3:25	0.80 0.84 0.80	2230	12.0 13.2	4.2 4.4 4.4		51	19.3	47.9		
6	3:35 to 4:05	0.80 0.80 0.86	2200	12.0 11.4	4.6 4.6 ① 5.0		50	17.7	47.1		
7								16.7	47.8		

① No run possible with such a varying CO_2 content.
Boiler House thinks this is due to the varying load.

② H. F. [illegible]

③ [illegible]

7 ft^3 [illegible] / 750

1.22 ft^3

$\frac{1}{0.64} \times 70$

[illegible]

1.22 ft^3 / lb.

1,000 →

110 ft^3 co.

$\frac{\text{[illegible]}}{50}$

5% CO_2 from 50 cu ft 1.22

17½ cu ft =
4
7 cu ft per ton

7 × 17.5

122 cu ft p. hr.

122,000 per hr.

2000 cu ft per min

70% abs. eff

17 117

50 cu ft p hr

$153.00

1 absorber 750 gals

Intake suction

Exp.

Large

absorber 50 cu ft p hr.]
Cap 2.5 gals]

750 gals. 15
75

300 Tonnes
50
15000 cu ft p hr.

10 Ton plant
10 units

50 H

13 liter unit
11 liter unit
7.5 l 4 gal unit

5.5" H_2O suction

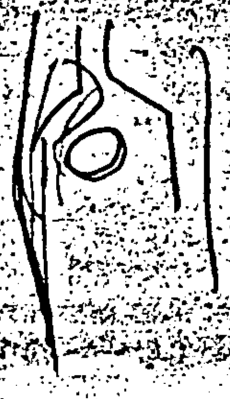
10½" Hg = 140" H_2O

?

1 gal = 20 cu ft

7
2.5 gals cap 50 cu ft 750
15,000 cu ft =

10 1 gal = 20 cu ft p h
7.5 75
1500 cu ft.



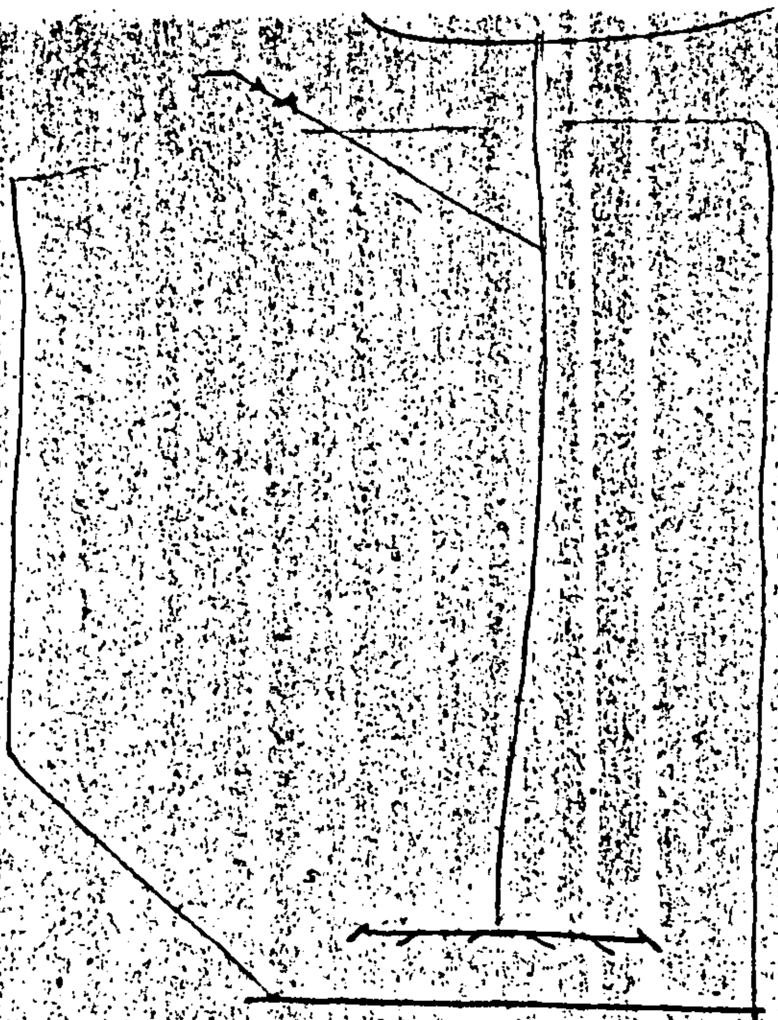
minimal
no fabrication
except for top
no pumping

11.0% CO2 down
to 4.4% CO2

lbs CO2/gal
= 0.2

5 probable max. H.P.
= 75

6 duplication of results
on large scale
> ?



small
fabrication

power primary
required (01?)

15.0% CO2
and 20.0% CO2

in CO2/gal CO

+5.0 - 400.

scale (toward this end the injections) carried out the following should be ~~[illegible]~~

1. Try the absorption in a 750 gal unit — either at Denver or here

√ 345

~~2. Buy a~~
2. Buy a 75 gal unit (complete with a 1 h.p. motor) & try the absorption here

variables

power consumption

a - programming

b - alarm

c - speed

75

[illegible]

[illegible]

[illegible] × 8.5 = 102,000 ft³/h

$\frac{102,000}{60} \times 2.5 = 5000$ gals

= ~~6.8 minutes~~

7 minutes

$$\frac{\begin{array}{r}46.8\\34.6\end{array}}{12.2}\Big/46.8 = 26.0\% \times 24.8 = 6.4 \text{ gms Na}_2\text{CO}_3$$

conv to $NaHCO_3$

plus $\frac{\begin{array}{r}49.4\\46.8\end{array}}{2.6} \times 0.053 \times \frac{110}{10} \to 1.4$

$\overline{7.8}$ gms Na_2CO_3 conv to $NaHCO_3$

$$\frac{\begin{array}{r}43.5\\31.2\end{array}}{12.3}\Big/43.5 \to 28.2\% \text{ NaHCO}_3 \times 23.1 = 6.5 \text{ gms Na}_2\text{CO}_3$$

conv to $NaHCO_3$

$$\frac{\begin{array}{r}48.9\\43.1\end{array}}{5.8} \to$$

3.1 gms Na_2CO_3 conv to $NaHCO_3$

$\overline{9.6}$

1.8 gms Na_2CO_3

$11.8 - 4.0 \rightarrow 7.8$ / 70

$\frac{.07 \times 8}{8.5} \times 2.0 = 0.64$ lbs. co. / hr

per $2\frac{1}{2}$ gals

per 1.0 ton basis

$\frac{20,000}{24} \Big| \frac{\text{lbs} / \text{hr}}{} \Big| = 833$ lbs / hr

~~0.64~~

$\frac{3250 \text{ gals}}{750}$ $\longrightarrow$ $\frac{833}{0.64} \Big| \frac{2.5}{} =$

5 units

1,400
1100

2500 × 5

12,500 cost for absorbers

~~[illegible]~~ 3,000
2000

Settler 5,000

Decanters

Scrubber 5,000

~~[illegible]~~

3,000

Instruments 2000

Heat Exch 1000

Liq Pumps

31,000

Gas Flow

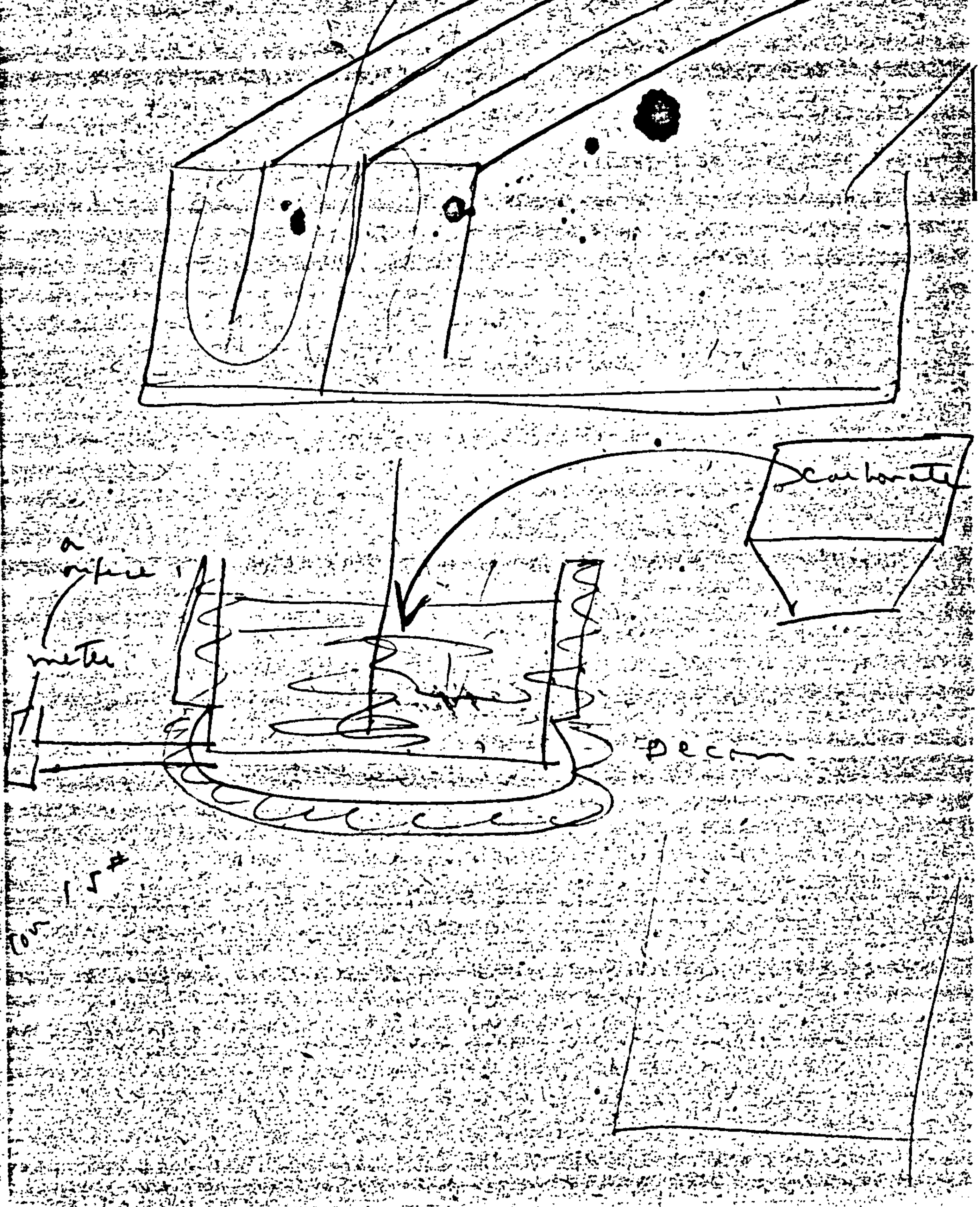
CO2 ~~[illegible]~~ Recorders.

SO2 Recorders.

Steam meters

Wattmeters

measure (stage for decomposition



4/30/41.

R U N #3

Data Sample No.	Time	Gas Rate C.F.P.M.	Speed r.p.m.	Gas Analysis % CO_2			Temp °C	Titration ml. of N H_2SO_4			
				Inlet	Exit orsat	Corrected Exit		Solution		Total	
								o.o.	m. o.	o.o.	m. o.
1	1:45	0.50 (1)	2050	11.0	3.8		46				
2	2:00	0.70 (2)	2050	11.0	5.8		47				
	2:15	0.60 (3)	2050	11.6	6.2		50				
4	2:30	0.60 (4)	2040	11.6	6.0		51				
5	2:45	0.60 (5)	2100	11.0	6.2		51				
6	3:00	0.60 (6)	2100	11.0	6.0		50				
7 (9)	3:30	0.90 (7)	2270 (11)	11.0	8.0		49				
8 (10)	4:30	0.75 (8)	2250	12.0% (?)	1.6 (?) 5.2		50				

Notes:-

(1) - 8 liters
(2), (3), (4), (5), (6), (7), (8), - 10 liters.
(9) - Inlet valve wide open.
(10)- No pump, just Denver suction.
(11)- Suction = 10.5 " Hg.

Continued

Results:-

1. By the use of standpipes, 10 liters were kept in the absorber. This was done even with a gas rate as high as 54 ft.^{3}/hr.

2. The rotor speed was too low (2050 r.p.m. as compared with previous values of 2300 to 2400 r.p.m.) This was thought due to the partial closing of the inlet valve in regulating the gas flow.

3. With the above conditions an average inlet gas of 11.0% CO_2 and an exit of 6.0% CO_2 were obtained. The gas rate was 36 ft.^{3}/hr.

4. The suction pulled by the Denver was found = 10.5" Hg. and, therefore, it was decided to run the absorber just by the use of this suction. The data were:

   a. Speed 22.50 r.p.m.

   b. Gas Rate 45 ft^3/hr.

   c. Gas analyses % CO_2 } inlet 12.0
   exit 3.2 (1.6?)

Signed:

Harry Gold

Joseph E. P. Bowen

Witnesses

R. J. Baird

M. E. Dougherty

use of the Denver Flotation apparatus
as an absorber

3 spaces

[illegible] (Run [illegible]) [illegible] ⇌ [illegible] + H_2O

Sample no.	1	1(a)	2	3	4	5	6
Inlet, % CO2	12.0	12.0	12.0	12.0	12.0		
Outlet, % CO2	2.8	2.9 3.4	4.4	5.8	5.8		
Gas flow, C.F.M.	0.20	0.1(?) 0.15	0.20	0.21 0.05	0.20		
Temp, °C	30°	30°	30°	28°	26°		
S.G.	21.9 5.8%		21.1 9.0%	20.7 10.8%	20.1 12.4%		
M[illegible] %	46.1		46.4	46.4	46.4 → 44.6 gms.		
Time	10:25	11:00		11:30	12:00		

The run was stopped because the temperature of the solution was too low; all previous work on absorption had been done at 45-48°C

Sample no.	1	2	3	4	5	6	7
Time	1:15	2:15	2:45				
Inlet, % CO₂	12.6	12.0 12.3	12.0				
Outlet, % CO₂	10.0	7.6 8.8	4.4				
Gas flow, c. ft/min.	0.21	0.20	0.15				
Temp., °C	35	41	46				
O.C.	22.2 4.9%	21.4 8.7%	20.6 12.9%				
M.O.	46.7	46.9	47.1				
absorber amps: motor	[illegible] 24.8 amps		1012				
absorber amps: rotor	2 Nov '65		780				
pump amps: motor			890				
pump amps: pump			1900				

The poor absorption may be due to the fact that the agitation did not seem as vigorous as ~~in~~ Run #1. This could possibly have been caused by the "Calrod" heater being on the same line as the motors on the absorber and the pump.

Sample	1	2	3	4
Amt. Na2CO3 [illegible]	1.2	2.2 1.2 1.0	2.7 2.2 0.5	3.3 2.7 0.6
Amt. CO2		0.112	0.21	0.25
[illegible] CO2 Titration factor 1.0248		0.025	0.013	0.01
% CO2 abs. <u>orsat</u>		9.1	7.6	6.[illegible]
% CO2 abs. <u>Titration</u>		4.0	3.7	2.[illegible]
Excess air by orsat		2.9	4.4	5.[illegible]
Corrected excess air		8.0	8.3	9

Sample	1	2	3
NaCl [illegible]	1.2	2.2 1.2 1.0	3.2 2.2 1.0
[illegible] CO2		0.42	0.42
[illegible] Titration factor = 0.0525		0.025	0.025
[illegible] direct		3.5	7.6
[illegible] Titration		4.0	4.0
[illegible] by direct		8.8	4.4
[illegible]		8.3	8.0

Changed [illegible] 9-1 [illegible] No. [illegible] Boiler Room
at start

Run #4

ate → mple No.	Time	Gas Rate, c.f.p.m.	Speed, r.p.m.	Gas Analyses, % CO₂			Temp, °C	Titration, ml. of N H₂SO₄			
				Inlet	Exit (Orsat)	Corrected Exit		Solution		Total	
								[illegible]	M.O.	[illegible]	M.O.
① 1	10:30 to 11:00	0.90 0.85 0.90	2170	10.0	3.8 4.2 4.6		48	24.4	49.0		
2	11:00 to 11:30	0.90 0.90 0.90	2200	11.6	4.6 4.8 5.2		48	22.5	48.5		
3	12:45 to 1:15	0.90 0.90 0.85	2200	11.2	0.6 0.6 0.6		49	21.1	48.6		
4	1:15 to 1:45	0.90 0.95 0.85	2250	10.2	4.4 4.6 4.6		49	21.1	48.6		
5	1:55 to 2:25	0.90 0.90 0.90	2240	10.4	5.4 5.0 5.4		50	20.3	48.4		
6	2:35 to 3:05	0.90 0.90 0.90	2240	11.4	5.6 5.6 5.8		49	19.7	48.9		
7	3:10 to 3:40	0.90 0.70 0.65	2240 2110 2120	11.4	5.0 3.0 3.6		50	18.9	48.8		
8	3:46 to	0.90	2230	11.4	2.8		51	18.3	48.6		
8(a)	4:06	0.90	2230	11.4	2.8		51	18.5	47.8	18.1	48.8
9	[illegible]							19.1	49.0	17.0	48.6
9(a)	4:35	0.85 0.90 0.90	2230	9.2	2.3 2.2 2.4		51	17.9	49.4	18.2	49.9

Run #3

Data → Sample No.	Time	Gas Rate, c.f.p.m.	Speed, r.p.m.	Gas Analysis, % CO_2			Temp., °C	Titration, ml. of N H_2S[illegible]			
								Solution		Total	
				Inlet	Exit (orsat)	Corrected Exit		P.P.	M.O.	P.P.	M.O.
1	1:45	0.50 ①	2050	11.0	3.8		46				
2	2:00	0.70 ②	2050	11.0	5.8		47				
3	2:15	0.60 ③	2050	11.6	6.2		50				
4	2:30	0.60 ④	2040	11.6	6.0		51				
5	2:45	0.60 ⑤	2100	11.0	6.2		51				
6	3:00	0.60 ⑥	2100	11.0	6.0		50				
7 ⑨	3:30	0.90 ⑦	2270 ⑪	11.0	8.0		49				
8 ⑩	4:30	0.75 ⑧	2250	? 12.0%	11.6(?) 3.2		50				

Notes

① – 8 liters

②, ③, ④, ⑤, ⑥, ⑦, ⑧ – 10 liters

⑨ – Inlet Valve wide open

⑩ – No pump, just Denver suction

⑪ – Suction [illegible] 5" Hg

Results

By the use of standpipes, 10 liters were kept in the absorber. This was done even with a gas rate as high as 54 ft³/hr.

2. The rotor speed was too low (2050 r.p.m. as compared with previous values of 230 to 2400 r.p.m.). This was thought due to partial closing of the inlet valve in regulating the gas flow.

3. With the above conditions an average inlet gas of 11.0% CO_2 and an exit of 6.0 CO_2 were obtained. The gas rate was 36 ft³/hr.

4. The suction pulled by the Denver was found = 10.5" Hg and therefore it was decided to run the absorber just by the

use of this section, the data were

a. Speed 2250 r.p.m.

b. Gas Rate 45 ft³/hr.

c. Gas analyses, % CO₂ { Inlet 12.0
{ Exit 3.2 (1.6?)

Signed:

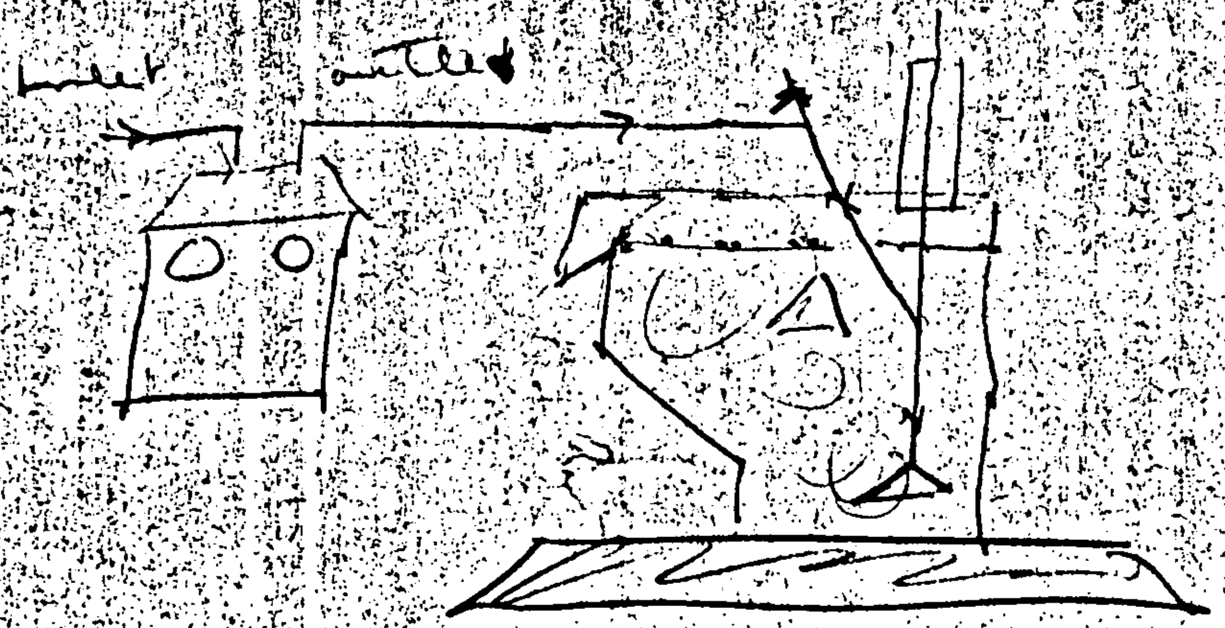
Harry Gold
Joseph E. B. Bowen

Witnesses:

M. E. Dougherty
R. J. Baird

Run #6

ata → mple No. ↓	Time	Gas Rate c.f.p.m.	Speed, r.p.m.	Gas Analysis, % CO_2			Temp., °C	Titration, ml. of N H_2S			
								Solution		Total	
				Inlet	Exit (orsat)	Corrected Exit		o.c.	M.O.	o.c.	M.O
1	1:30							19.8	46.2		
2	2:00	0.20	1520	12.2	2.4	4.5	49	17.9	46.0		
3	2:30	0.21	1560	12.3	3.9	7.9	49	16.6	45.8		
4	3:00	0.21	1550	12.0	5.7	8.1	49	15.6	45.8		
5	3:15	0.22	1560	12.2	5.6	6.3	49	14.9	46.0	15.2	42.
6	3:30							16.1	43.2	15.8	46.
6	4:00	0.22	1550	12.0	4.3	4.7	50	14.6	41.2	14.0	46.



2900 cc

Recovery of CO_2 from Flue Gas

VI Use of the Denver Flotation apparatus as an absorber

Report #1

Summary

The work was carried out on a 3 liter size apparatus. If comparable results can be obtained on a larger scale, then the equipment has a distinct possibility for use as an absorber. Translated to the basis of a standard (size?) 6 cubic foot unit, one such would produce 2 tons of CO_2 per 24 hours.

The following facts were also uncovered.

1) A certain minimum speed is necessary — below this the absorption is so poor as to make the machine worthless.

2) about a fluid gas rate of 15 ft³

per gal soln per hour, both the absorptive efficiency and the lbs CO_2/gal soln/hr fall off rapidly

3. Since the apparatus develops a suction of 5" H_2O, no power would be needed to force the flue gas through the liquid.

Problem: To obtain qualitative an
quantitative data on the [illegible]
apparatus so that the possibilit
of using this equipment as a
absorber may be determined.

Description of Apparatus: The [illegible]
(as shown in the diagram)
was set up near a source of
flue gas (in ch. Hse #2). A 4 lit
aspirator bottle was used to
wash out the fly ash and SO₂.
The gas was drawn in by mean
of the a small displacement pump
It then passed in succession thr
the gas meter and into the ab
The rate of flow was controlle
by means of a by-pass and a
screw clamp. Connections we
also made for taking of sample
[illegible] without creat

a back pressure. For the outlet samples were collected by means of a funnel and a small bottle. Two turns of "Calrod" were used to keep the solution at the proper temperature.

Procedure: a solution containing approximately 25 gms. Na_2CO_3/100 gms. H_2O (but accurately analysed) was used for the carbonation. The rotor was started and the flue gas passed in under the following conditions

Run nos.	Flue gas, ft³/hr	Rotor speed	ml. Conc.
1, 2, 3	12	780	2900 2900 2800
4	12.0	1340	2800
5, 6	12, 13.2	1550	2700 3300
7	19.8	1560	3200
7(a)	17.0	1560	3200

In all except run #7(a) the flue gas was used as it came from the [illegible] with 12.9% CO_2; stacks, in this last case, however, air was mixed with the incoming gas so that the % of CO_2 was lowered to 7.97. This was done a followup of run #7 & was {so as} to see what absorption would be be obtained using a increased gas rate and two units in series.

The effect of varying rotor speed was tested in runs nos. 1, 2, 3, and 4.

A change in the capacity of the unit was made for runs nos. 6, 7, and 7(a) by putting a plate across the overflow; the volume of liquid which could be used was thus increased from 2700 to 3300 ml.

The % of CO_2 in the inlet and exit gas was determined by an

was further checked by titration
of samples of the liquid and

Run #1

Data → ample No. ↓	Time	Gas Rate, c.f.p.m.	Speed, r.p.m.	Gas Analyses, % CO₂			Temp., °C	Titration, ml of N H₂SO₄			
								Soln.		Total	
				Inlet	[illegible]	[illegible]		O.C.	M.O.		
1	10:45		780				30	21.9	46.1	21.9	46.1
2	11:00	0.15	780	12.0	2.9	8.0	30	21.1	46.4	21.1	46.4
3	11:30	0.20	780	12.0	4.4	8.3	28	20.7	46.4	20.7	46.4
4	12:00	0.205	780	12.0	5.8	9.9	26	20.1	46.4	20.1	46.4

Run #2

1	10:45		780				35	22.2	46.7		
2	2:15	0.205	780	12.3	8.7	8.3	41	21.4	46.9		
3	2:45	0.15	780	12.0	4.4	8.0	46	20.6	47.1		

Run # 3

Data → Sample No. ↓	Time	Gas Rate, c.f.m.	Speed, r.p.m.	Gas Analysis, % CO₂			Temp., °C	Titration, ml. of N H₂SO₄			
								Solution		Total	
				Inlet	Exit by Orsat	Corrected Exit		o.c.	M.O.	o.c.	M.O.
1	10:45							23.5	47.6		
2	11:15	0.20	770	11.9	4.7	7.2	49	22.5	47.4		
3	11:45	0.20	780	12.4	3.6	9.7	49	22.0	47.8		
4	500 ▲ 11:50	0.20	780	12.4	2.9	9.4	50	21.6	48.9		
5	2:00	0.20	785	12.4	3.6	11.3	50	21.3	49.0		
6	2:10	0.20	790	12.4	4.8	10.7	50	20.8	49.0		
7	3:00	0.20	790	12.0	5.4	10.0	48	20.5	49.6		
8	3:15	0.18	780	12.2	5.2	10.9	50	20.3	49.5		

Run #4

ata → ample No. ↓	Time	Gas Rate, c.f.p.m.	Speed, r.p.m.	Gas Analysis, % CO_2			Temp., °C	Titration, ml of N H_2SO			
				Inlet	Exit (orsat)	Corrected Exit		Solution		Total	
								O.C.	M.O.	O.C.	M.O
1	1:30							21.2	46.4		
2	2:00	0.20	1270	12.0	3.7	6.2	46	19.4	46.8		
3	2:30	0.20	1290	12.2	6.2	8.1	49	18.0	46.2		
4	3:00	0.20	1290	12.2	6.2	7.5	51	16.5	45.6		
5	3:30	0.20	1320	12.2	6.6	8.4	50	15.4	45.2		
6	3:45	0.20	1340	11.7	6.5	6.8	50	15.3	42.0	14.8	45.
7	4:15						49	16.1	45.1	16.2	45.
7(R)	4:45	0.20	1340	11.3	4.7	6.6	50	15.4	42.3	15.0	46

Run # 5

fa→ mple, No.↓	Time,	Gas Rate, c.f.p.m.	Speed, r.p.m.	Gas Analysis, % CO_2			Temp., °C	Titration, ml of N H_2S			
				Inlet	Exit (orsat)	Corrected Exit		Solution		Total	
								o.c.	M.O.	o.c.	M.O.
1	10:45						50	20.0	45.5		
2	11:15	0.20	1520	12.1	3.4	4.6	50	18.0	45.6		
3	11:45	0.20	1830	11.8	5.2	6.3	51	16.3	45.5		
4	12:15	0.20	1570	12.3	5.9	7.2	49	14.3	45.4		
5	12:30	0.22	1550	12.2	6.6	8.2	53	14.2	45.2		
6	12:45	0.23	1500	11.9	7.2	5.6	52	15.9	40.8	13.3	45.8
7	11:00 to							16.7	43.0	15.1	45.5
7(a)	11:30	0.21	1550	12.1	5.6	5.2	48	16.1	41.2	13.2	45.6

Runs Nos. 7 and 7(a)

Data → Sample No. ↓	Time	Gas Rate, c.f.p.m.	Speed, r.p.m.	Gas Analysis, % CO2			Temp., °C.				
				Inlet	Exit (Orsat)	Corrected Exit					
1	10:15										
2	10:45			12.2	1.0						
3	11:15			12.1	4.1						
4	11:45			12.0	4.5						
5	1:45			12.0	3.8						
6	1:45 to 2:00			12.1	6.6						
7	3:15 to										
7(a)	3:45			11.8	4.4	8.0					
8	4:00 to										
8(a)	4:30			7.9	3.0	5.3					

2.5003 g Na_2CO_3

$45.04 \times 0.0530 \times N = 2.5003$

$N = 1.046$

$23.\cancel{00} \times \overset{4.6}{\cancel{0.0476}} \times 0.053 = \frac{5.619}{0.049} = 114$ cc

$\frac{60}{9} \times 0.05$

$9\overline{)3.0}$

0.3

1.16.50

Run #7 (cont'd)

Sample #	7 new start				7(a)	8 (+ [illegible] NaClO$_3$)				8C
Time	3:15	3:25	3:30	3:40	3:45	4:00	4:10	4:15	4:20	4:
Inlet	8.0	8.0	7.0	8.0	8.6	12.2	12.2	12.4	11.0	1
	7.9 ave.					11.8 avg				
Outlet	2.4	2.6	2.8	3.2	4.0	4.2	4.8	4.2	4.6	4
	3.0 ave.					4.4 avg				
Rate, l.p.m.	0.30	0.30	0.30	0.30	0.30	0.30	0.33	0.33	0.33	0.
Temp, °C	49	50	50	49	49	49	51	52	52	5
Speed, r.p.m.	←		1560			→				
[illegible] O.C.	18.7 (24.39%)				17.7 (28.49%)	18.2 (25.69%)				16. (31.69%)
M.O.	49.4				49.4	48.9 ≈ 48.9 gms.				48.
[illegible] O.C.	18.2				17.8	19.3				17.
M.D.	47.3				46.4	47.1				45

Run 7

Sample	1	2	3	4
[illegible] Na₂CO₃ conc	0.3	2.5 0.3 2.2	4.0 2.5 1.5	5.6 4.0 1.6
[illegible] CO₂		0.91	0.62	0.[illegible]
[illegible] CO₂ Titration (factor 0.0661)		0.066	0.041	0.044
% CO₂ abs. Orsat		11.2	8.0	7.5
% CO₂ abs. Titration		5.7	3.9	4.2
Calibration by [illegible]		1.0	4.1	4.5
Corrected [illegible]		5.5	8.2	7.8

5	6	7	7(a)	8	8(a)
6.7	7.5		7.5		8.2
5.6	6.7	6.5	6.5	6.6	6.6
1.1	0.8		1.0		1.6
0.46	0.33		0.12		0.66
0.030	0.022		0.028		0.044
8.2	5.5		4.9		7.4
2.9	4.2		2.6		3.8
3.8	6.6		3.0		4.4
9.1	7.9		5.3		8.0

Idea for Table Data?

Column

Time

Rate, c.p.m.

Temp, °C

Cumul'd c.p.m.

dilutions
- Initial
- Initials
- Corrected initial

0.1 gm → 1,000 c.c.

100 γ/cc

2.5 → 0.05 γ

0.02 γ/cc.

Sample #	1	2	3	4
Time	10:45-11:18	11:15-11:45	1100-1130	1130-1200
Inlet	11.9 11.6 12.2	12.4 12.4	12.4 12.4	12.4 12.
Outlet	1.7 1.0 4.4 2.8	3.6 3.8 3.4	2.9 2.6 3.2	3.6 3.6
Rate	0.20	0.20	0.20	0.20
C.F.M.				
Motor	1180	1290	1210	1210
Rotor	770	780	780	785
Temp. °C	49	49	50	50

Speed

11.6
11.9
12.2
3)35.6
11.9

1.0
1.4
2.8
5.2
1.7

10.4

12.4
3.6
8.8

Run #1 (cont'd)

Sample #	5	6	7
Time	2:00-2:20	2:00-3:00	3:00-3:15
Inlet	12.[illegible] 12.4	12.0	12.2
Outlet	4.8 4.7	5.4	5.2
Rate cfm	0.20	0.20	0.18
Cond. Inlet	11.80	1220	1240
Cond. Outlet	790	790	780
Temp. °C ambient	50	48	50

Titrations

47.6
47.0
0.6
1.3 %

1 — O.C 23.5
M.O 47.6

47.4
45.0
2.4
1.3 g NaHCO3
NaHCO3
5.1 % NaHCO3

O.C 22.5
2 — M.O 47.4

47.8
44.5
3.3
2.1 g NaHCO3
NaHCO3
3.7 % NaHCO3

O.C 22.0
3 — M.O 47.8
25.8

O.C 21.6
4 — M.O 48.2
11.9 %

O.C 21.3
5 — M.O 49.0
13.1 %

O.C 20.8
6 — M.O 49.0
15.1 %

O.C 20.5
7 — M.O 49.6
13.3 %

O.C 20.3
8 — M.O 49.5
18.0 %

Total Na [illegible]

[illegible] 0.08 [illegible] = [illegible]

[illegible] Na₂CO₃

[illegible]

[illegible] = [illegible]

[illegible] 1.3 [illegible]

and

[illegible] 0.073 = [illegible] Na₂CO₃

[illegible] Na₂CO₃

[illegible] Na₂CO₃

[illegible] = [illegible]

[illegible] Total

0.415 [illegible] = [illegible]

[illegible]

[illegible] = [illegible]

0.0213 [illegible] 85 [illegible] = 0.0213 [illegible] CO₂

0.215 [illegible] 100 = 3.670
6.0

11.9
3.6
8.3 [illegible]

[illegible] → 0.39 [illegible]

[illegible] 0.30 × 0.415 = 0.332 [illegible] CO₂

0.220 [illegible] 300 [illegible] 100 [illegible] = 0.0133 [illegible]

[illegible]

0.60 [illegible] 30 [illegible] 31 [illegible] 100 [illegible] 84 [illegible]

0.0142 [illegible] 0.163 [illegible] 9.670 [illegible]

[illegible] 3

Sample	1	2	3	4
[illegible] Na₂CO₃ [illegible]	0.3	1.3 0.3 1.3	2.1 1.3 0.8	1.0 0.1 0.9
[illegible] CO₂		0.54	0.33	0.7
[illegible] CO₂ titration factor = 0.0875		0.035	0.019	0.021
% CO₂ after [illegible]		10.2	8.8	9.5
% [illegible] after titration		4.7	2.7	8.0
Cor. [illegible] by [illegible]		1.7	3.6	7.9
Corrected [illegible]		7.2	9.7	9.4

5	6	7	8
3.3	3.8	4.4	4.6
3.0	3.3	3.8	4.4
0.3	0.5	0.6	0.2
0.15	0.21	0.25	0.08
0.0074	0.012	0.014	0.0046
8.8	7.6	5.6	7.0
1.1	1.7	2.0	1.3
3.6	4.8	5.4	5.2
11.3	10.7	10.0	10.9

6/6/15

Run

Sample #	1	2	3	4	5
Time	1:30	2:00 p.m. 1:30	2:10 0-3:00	3:00 0-3:00	1:05.0 [illegible]
Inlet	12.0 12.0	12.2 12.0 12.4	12.2 12.4	12.4 →	11.8
Outlet	3.7 3.4 4.0	6.2 6.4	6.2 6.4	6.2 →	6.6
Rate of flow	0.20	0.20	0.20	0.20	0.22
Temp	46	49	51	50	50
Cond	1270	1290	1290	1320	1340
O.C	21.2 91.90	19.4 17.19	18.0 4.170	16.5 17.79	15.4 81.8
[illegible]	46.4	46.8	46.2	45.6	45.2

4

24.6 gms Na₂CO₃

Sample #	7 ([illegible])		7a		6
Time	4:15	to	4:45		
		11.3			
[illegible]	10.6	11.4	7.6	11.4	8.4 7.6 5.2 5.0
			4.7		
[illegible]	2.2	3.8	2.4	6.4	4 2.6.2
	7.4	7.6	5.2	5.0	6.5
Rate	0.20	0.20	0.20	0.20	11.6 [illegible]
[illegible]	4.9	4.8	4.9	5.0	
[illegible]	13.40				
	16.2		15.0		14.8
		29.0%		34.9%	
0.5 19.0	45.6 13.2	7.1 [illegible]	46.1 ([illegible]) 10.0 16.1	8.5 [illegible]	45.2
0.5	16.1		15.4		15.3
19.0	43.1		42.3		42.0

(Run # 4)

$1.4 \times 0.415 = 0.581$ gms CO_2

$$\frac{0.581}{} \left| \frac{\overset{\text{gms } CO_2}{2700}}{100} \right| \frac{\overset{\text{Total gms } CO_2}{}}{454} = 0.0345 \text{ lb } CO_2$$

CO_2 by gas analysis

$$\frac{6.0}{} \left| \frac{\overset{\text{Total ft}^3}{5.2}}{100} \right| \frac{\overset{\text{ft}^3\ CO_2}{}}{8.5} = 0.0367 \text{ lb } CO_2$$

$0.0345 \times 8.5 = 0.293$ ft³ CO_2

$\frac{0.293}{6.0} \times 100 = 4.9\%$ CO_2 absorbed

$$\frac{2800}{3800} = 0.737 \text{ gal}$$

$$\frac{0.033 \times 2 \text{ lb } CO_2}{0.737 \text{ gal soln}} = 0.103 \text{ lbs per gal soln}$$

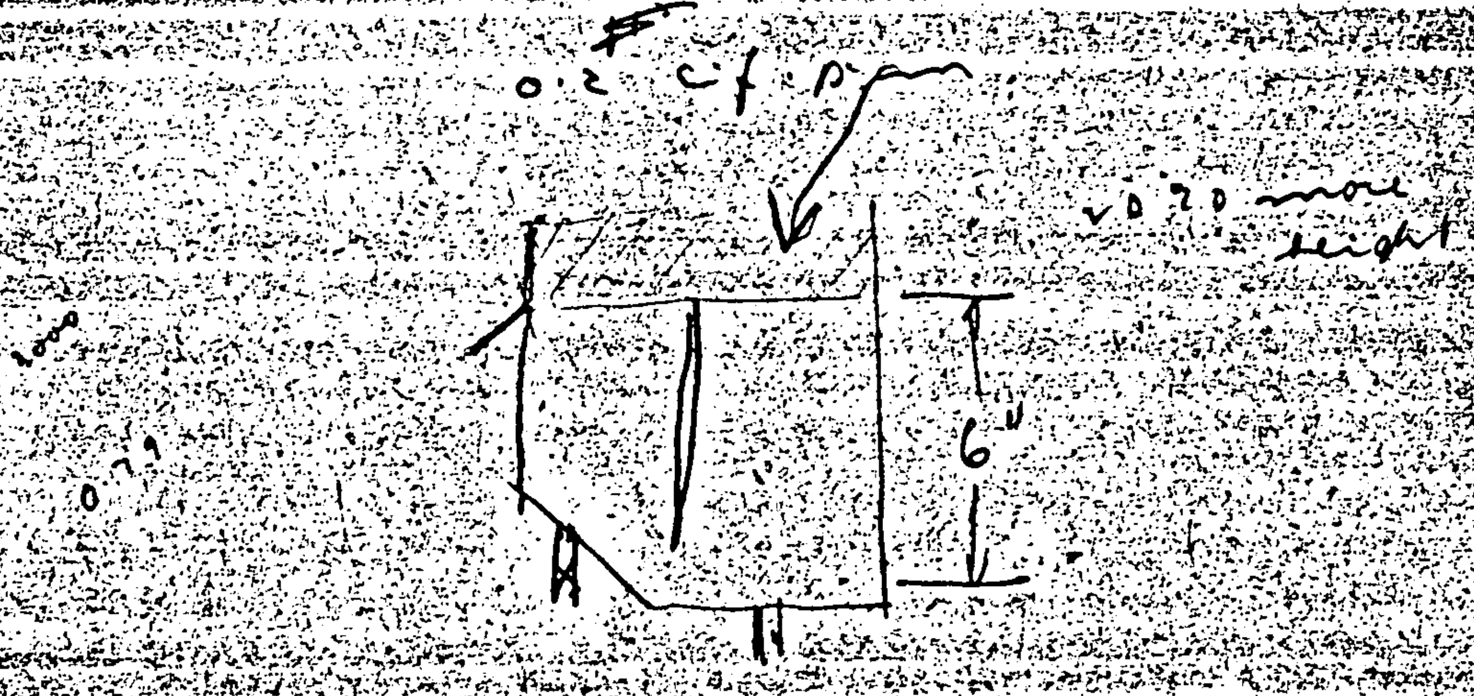
$= 1555$ lbs CO_2 / unit / hr

$= 3770$ lbs. CO_2 / unit / 24 h

11.6

Excl gas 6.470 CO_2 $\quad \frac{5.2}{11.6}$

$= 4.570$



[illegible]		2	3	4
[illegible]	2.2	4.2 2.2 2.0	5.4 4.2 1.2	6.8 5.4 1.4
[illegible]		0.33	0.50	0.58
[illegible] Titration factor = 0.0573		0.048	0.049	0.033
[illegible]		8.3	6.0	6.0
[illegible] Titration		6.8	4.1	4.7
[illegible]		3.7	6.2	6.2
[illegible]		5.2	8.1	7.5

5	6	7	7 (a)
7.8	8.5		8.5
6.8	7.8	7.1	7.1
1.0	0.7		1.4
0.42	0.29		0.58
0.024	0.017		0.033
5.2	5.1		6.6
3.4	4.8		4.7
6.6	6.5		4.7
8.4	6.8		6.6

9/1/79

April 4, 1941.

American Chemical Society News Service,
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Enclosed please find $1.00 for which kindly send me Set of Abstracts of meeting papers presented at meeting of the Society in St. Louis.

Thanking you, I am

Very truly yours,

PENNSYLVANIA SUGAR COMPANY

Harry Gold

HG:MH Chemical Department.

Sample	1	2	3	4
[illegible]	2.8	5.1 2.8 2.3	6.8 5.1 1.7	8 6. 1.
[illegible]		0.96	0.71	0.
[illegible] Titration from 0.0551		0.053	0.039	0.
% [illegible]		8.7	6.6	6
% [illegible] Titration		7.5	5.5	5
[illegible] by [illegible]		3.4	5.2	5
Corrected [illegible]		4.6	6.3	7

ae
6/6/5.

Summary of [illegible]
on Denver Flotation apparatus

Method → Data ↓	Run # 4	Run # 5	Turbo-mixer	Rectangular absorber
Rotor speed, r. p. m.	1340	= 5" H₂O 1550		
Inlet gas, % CO₂	11.6	12.1	13.6	
Outlet gas, % CO₂ (Orsat)	6.4	5.2	4.4	3.0
Outlet gas, % CO₂ (Titration)	6.7	5.37		
% CO₂ absorbed (Orsat)	5.2	6.9	9.2	
% CO₂ absorbed (Titration)	4.9	6.8		
Lbs. CO₂ / cu. ft. soln. / hr.	0.103	0.139	0.448	0.139
Lbs. CO₂ / cu. ft. absorber space / hr.	0.0796	0.107	0.130	0.124
Lbs. CO₂ / Denver unit / 24 hrs.	3770	5000	—	
Apparent absorption efficiency, %	45	56	68	71

ft³ CO₂ / hr 12.0 12.6

5

8.6
7.8

0.8

0.83

0.73

6.6

5.9

5.6

0.3

6

7.7

6.191

9.7
7.7

2.0

0.83

0.057

7.7

7.3

4.3

4.7

6/6/50

J ry Gold

June 30, 1938.

RECOVERY OF CO2 FROM FLUE GAS

IV. USE OF THE TURBO-MIXER AS AN ABSORBER

Forward:

The experimental work recorded here (in Report Nos. 1, 2 and 3) should not be taken as an absolute measure of the value of the mixers because no power readings could be made; this factor may possibly be prohibitive as a very high speed is necessary. However, a high power consumption for the mixers may be somewhat balanced by the fact that no pressure would be required to force the gas through the liquid.

The only bases of evaluation that could be taken then, are (1) the apparent absorptive efficiency as determined by the value of the entrance and exit gases and

(2) the lbs. CO2 absorbed/gal. of absorber volume -- and even this does not have any meaning.

USE OF THE TURBO-MIXER AS AN ABSORBER UNLESS THE INVESTMENT COST OF THE EQUIPMENT PER POUND OF CO2 IS KNOWN.

Report #1

Problem:

To try a series of Turbo-Mixers as an absorption unit and to obtain quantitative data so that the value of this apparatus may be determined.

Description of Apparatus:

Three Turbo-Mixers were set up in series (as shown in the diagram) in Pyrex Glass Jars of 9 liters capacity each. The drive was provided by a 1/2 HP, 1750 RPM motor and the use of a system of belts and pulleys. A board and two wooden horses were used as a support for the system. The rate of flow of the flue gas was recorded by a gas meter, and the % of CO2 in the entrance and exit gases was determined by an Orsat Apparatus. The details of the mixers are also given and the passage of the gas and the liquid through them. The red lines show the flow of the gas and the blue the passage of the liquid.

Procedure:

The complete apparatus was set up as shown and each of the glass jars was fitted up to the casing of the impeller with an Na2 CO3 solution, containing approximately 25 grams/100 grams H2O. This is equivalent to 5" in depth, or 45 liters of solution per mixer. Flue gas from the stacks was passed in counter-current to the flow of the liquid and determinations made of
(1) the % of CO2 in the entrance and exit gases.
(2) the rate of gas flow
(3) the temperature of the solution.

Samples of the solution were also taken and titrated later for carbonate and bicarbonate. The run was continued for 1 1/4 hrs. until a heavy precipitate of NaH CO3 was obtained.

TIME PM	GAS ANALYSIS % CO2		GAS FLOW c.f.p.m.	TEMP. °C.	TITRATION, ml N H2SO4				
					Solution		Total		
	Ent.	Exit.			o.c.	m.o.	o.c.	m.o.	REMARKS
3:00	11.6	6.0	1.50	34	23.4	46.8	23.4	46.8	Belts Slippi
3:15	11.6	5.2	1.50	43					
3:30	11.6	4.2	1.50	46					
3:45	11.6	4.2	1.40	49					
4:00	11.6	4.9	1.40	49					Motor Hot
4:15	11.6	5.0	1.70	48	16.4	43.0	14.1	46.9	Conti Gas Leaks

Material Balance:

Time, Hrs.	Lbs. CO2 by Gas Analysis	Lbs. CO2 by Titration	% Diff.
16	0.93	0.87	7

Discussion:

1. Data - This first run may really be considered as a "tune up". In spite of the gas leaks encountered and the difficulty in obtaining a uniform drive, a quantitative material balance shows no loss. However, the belts slipped badly and the average exit gas of 4.6 can be improved upon.

2. Results. The results obtained are tabulated below in comparison with those of the rectangular absorber.

FACTOR	TURBO-MIXER	RECTANGULAR ABSORBER
Average % of CO2 in Exit Gas	4.6	3.0
Apparent absorptive efficiency,%	60	81
Lbs. CO2 absorbed per gal. soln.	0.198	0.139
Lbs. CO2 absorbed per gal. absorber space	0.104	0.124

No conclusions should be drawn from these figures; they are merely given so that a preliminary idea of the relative values may be obtained.

Basis: 1 hr.

Harry Gold

June 30, 1938.

USE OF THE TURBO-MIXER AS AN ABSORBER

Report #2

Problem:

To continue the work using a series of Turbo Mixers as an absorption unit; toward this end it is necessary to set up the apparatus so that more exact information may be obtained.

Description of Apparatus:

The assembly is the same as was used in Report #1, except that an effort was made to cut down the leaks by putting in a new gasket of softer rubber between the jar and the body plate of the mixer.

Procedure:

No change was made from the method used in Report #1, aside from "time outs" of one hr. or more after each 30 minute period of operation to

1. patch leaks
2. take samples of the solution
3. add fresh alkali when necessary.

Considerable slippage was still encountered with the belts, expecially after the mixers had run for 20 minutes in each period of operation. More complete data was taken than in Report #1, particularly on the Na2 CO3 soln. As was mentioned above, when precipitate appeared, the carbonate content of the solution was raised by the replacement of 2 liter portions of the slurry by fresh Na2 CO3 solution at 1/2 hr. intervals. The gas flow ranged between 1.20 and 1.75 c.f.p.m. but for the most part was kept fairly constant at 1.50 c.f.p.m. - the upper and lower limits were to test the effect of varying rates. The total actual time for the run was 2 hrs.

DATA

Time PM	Gas Analysis % CO2		Gas Flow c.f.p.m.	Temp. °C.	Titration, ml. N H2SO4				Remarks
					Soln.		Total		
	Ent.	Exit.			o.c.	m.o.	o.c.	m.o.	
3:25	13.0	4.2	1.55	45	24.0	48.0	24.0	48.0	
3:40	13.2	4.4	1.55	47					
3:55	14.0	5.2	1.60	49	19.9	47.3	19.9	47.3	1/2 hr. operation
5:00	14.0	6.0	1.75	45					
5:20	13.2	5.4	1.45	49					ppt.
5:30	13.2	4.6	1.45	49	16.8	44.7	16.8	47.5	1 hr. operation
6:10	14.0	4.4	1.50	46					+2 l. Na2 CO3 soln.
6:25	13.2	4.0	1.40	48					
6:40	13.9	4.4	1.20	49	14.4	39.2	14.2	48.4	1 1/2 hrs. operation
1[illegible]00	14.1	5.8	1.75	50	15.7	41.4	15.2	47.6	+ 2 l. Na2 CO3 soln.
11:15	14.0	4.8	1.30	50					
11:30	13.8	4.3	1.50	50	11.8	33.9	10.7	47.8	2 hrs. operation

Material Balance -

Time Hrs.	Lbs. CO2 by Gas Analysis	Lbs. CO2 by Titration	% Difference
1/2	0.48	0.46	4
1/2	0.46	0.39	18
1/2	0.41	0.39	5
1/2	0.48	0.49	2

Discussion:

1. Data - The check on the absorption by titration of the solution shows very little loss of gas by leakage. This, however, is due entirely to the pains taken to patch the bad spots and does not correct the inherent fault of the gasket and the warped body plate.

2. Results - These figures are obtained from the data after 1 1/2 and 2 hrs. of operation; that is, in both cases when precipitate was present as would be in the large scale recovery of CO2. The results for Report #1 are given and also those for the rectangular absorber.

Factor	Turbo-Mixer Report #1	Turbo-Mixer Report #2	Rectangular Absorber
Average % of CO2 in exit gas	4.8	4.4	3.0
Apparent absorptive efficiency, %	60	68	81
Lbs. CO2 absorbed per gal. soln.	0.198	0.248	0.139
Lbs. CO2 absorbed per gal. absorber space	0.104	0.130	0.124

These show that:

a. The apparent efficiency is not quite as good as that of the regular process, in fact it is 20% less, but this can be improved upon.

b. The mixers will absorb approximately 1 1/2 times as much CO2 per unit volume of absorbing solution as the rectangular unit, but this should be compared with the fact that,

c. For a series of mixers this figure is only 5% greater on the basis of CO2 absorbed per unit of absorber vol.

It was also discovered that increasing the rate of flow of gas above 1.50 c.f.p.m. (equivalent to 0.0675 f.p.m.) decreased the absorption considerably, so that the exit gas went up to 5.8% CO2.

Summary:

The mixers show a definite possibility for use as an absorption unit (this is not considering the limited field of the data obtained); on the basis of CO2 absorbed per unit vol. of absorber space it compared very favorably with the rectangular unit. The trouble encountered in continuous operation was still not ironed out, 'tho this only effects the small experimental apparatus.

June 30, 1938.

USE OF THE TURBO-MIXER AS AN ABSORBER

Report #3

Problem:

To continue the runs, using a series of Turbo-Mixers as an absorptive unit, with the purpose of

1. Improving the apparatus so that it would require less attention to leaks and the drive.

2. Determining the amount of CO2 removed by each mixer.

Description of Apparatus:

An attempt to eliminate the gas leaks was made by putting a heavy layer of litharge and glycerine between the top of the glass jar and the rubber gasket; otherwise the apparatus was the same as in Report #2.

Procedure:

The identical method was used as in the previous work and the absorption was continued until a precipitate appeared. Then 2 liters portions of the slurry were replaced by fresh Na2 CO3 solution and determinations made of the absorption in each mixer. The total time of absorption was two hours.

DATA

Time P.M.	Gas Analysis % CO_2		Gas Flow C.F.P.M.	Temp. °C.	Titration, ml N H_2SO_4				Remarks
					Soln.		Total		
	Ent.	Exit			o.e.	m.o.	o.e.	m.o.	
2:40	12.8	8.2	1.55	40	24.5	49.0	24.5	49.0	No speed
2:50	12.8	2.4	1.50	45					High speed
3:00	14.0	2.0	1.70	45					Leaks
3:10	14.0	1.0	1.80	45	21.4	49.3	21.4	49.3	Leaks; ½ hrs.
3:45	14.2	5.0	1.40	41					Low speed
6:00	14.0	3.8	1.70	48	19.1	49.2	19.1	49.2	3/4 hrs.
7:00	13.6	2.2	1.20	45					
7:15	13.7	2.4	1.20	45	17.6	44.5	17.2	49.4	1 hrs.
8:30	13.7	10.0	1.55	42					1st mixer & 2% Na_2CO_3
8:40	13.9	5.9	1.55	45					2d mixer
9:00	13.7	2.0	1.55	46					3d mixer
9:20	13.6	9.7	1.50	48					1st mixer & 2% Na_2CO_3
9:40	13.6	6.0	1.48	48					2d mixer
9:50	13.6	2.2	1.48	48					3d mixer 2 hrs.

Material Balance -

Time Hrs.	Lbs. CO2 by Gas Analysis	Lbs. CO2 by Titration	% Diff.
1/2	0.43	0.40	7
1/4	0.28	0.29	3
1/4	0.24	0.24	-

Discussion:

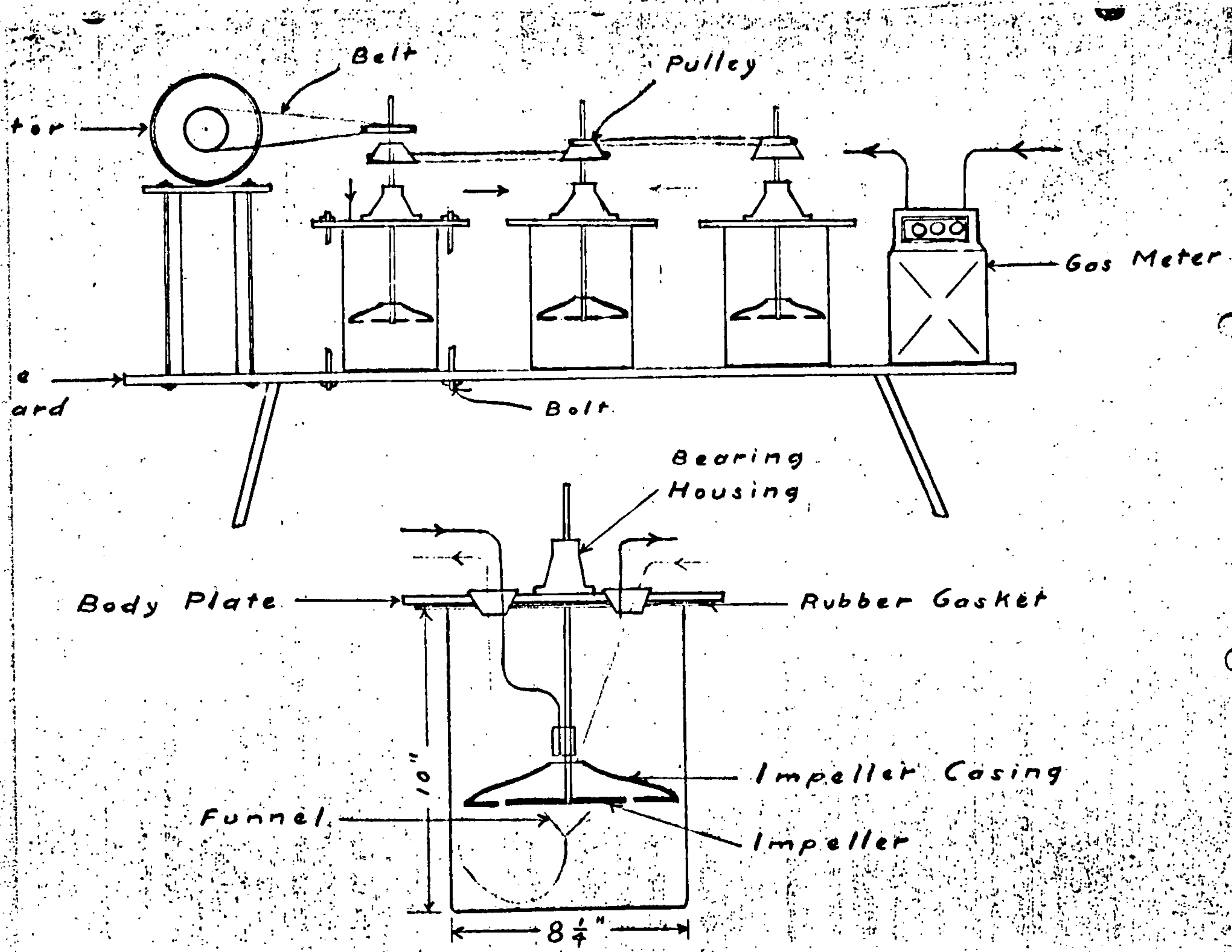
1. Data - The material balance on the absorption shows very little loss but the seal of litharge and glycerine blew out continually and time had to be taken to patch it. The difficulty was finally traced to the following sources:

a. The slight warping of the cast aluminum body plate.
b. The insufficient number of bolts (3) to pull down evenly on the body plate.
c. The need for a very soft rubber gasket of either pure or sponge rubber.
d. Especially, the lack of a by-pass for relieving the pressure when a sample of the exit gas is taken.

It was also decided that the drive could only be made more uniform by mounting the entire apparatus on a sturdier and more workmanlike base than heretofore used - makeshift devices had failed to correct the essential faults and the only reason the absorption was improved over the first two runs was due to the greater experience in operating the unit. The greatest troubles here are

a. The horses with the board across them form a support which is entirely too light and which has no real rigidity.

b. The shafts of the mixers were only fixed at one place - the bearing housing on the body plate - and as a result the pulleys on these shafts could be drawn together or apart almost as desired. This gave a very uneven tension on the belts with the consequent variability in the speed of the impellers.

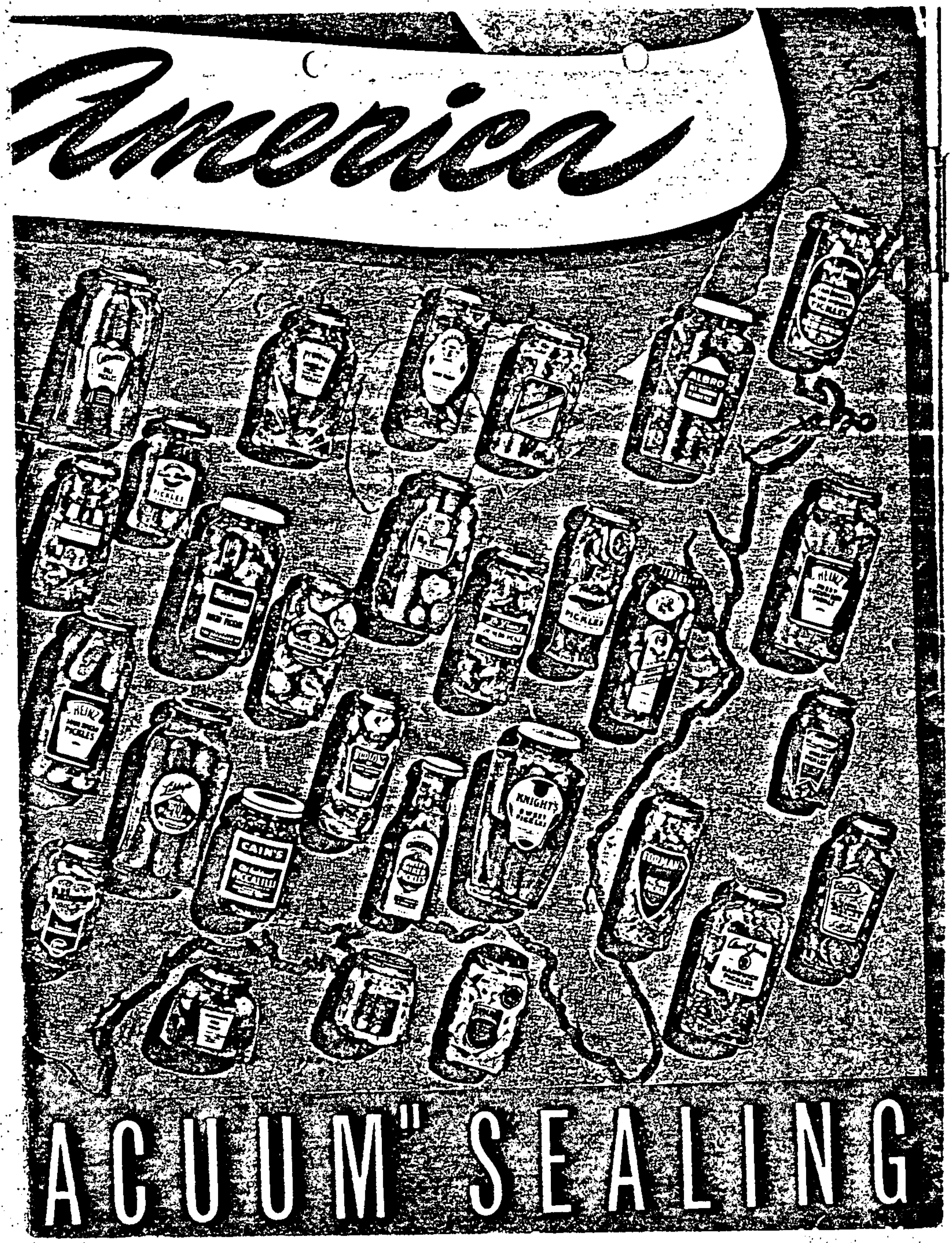

Belt
Pulley
tor
e
ard
Bolt
Gas Meter
Bearing Housing
Body Plate
Rubber Gasket
Impeller Casing
Funnel
Impeller
10"
8 1/4"

• Packers of pickles who send their brands to market "Vapor-Vacuum"* Sealed provide an *extra* service to the consumers of the nation: Their brands are always *fresh!*

But these packers also serve themselves. For not only do Vapor-Vacuum Caps insure against mold, fermentation, leakage and other temperature and oxidation hazards . . . they permit many production economies, as well.

White Cap Company engineers can undoubtedly show you, as they have so many leading packers, how installations for "Vapor-Vacuum" Sealing can help eliminate breakage, speed up operations and cut other production costs. Take advantage of this *free* consultation service, now.

*Trade Mark of The White Cap Company


America
ALBRO
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KNIGHT'S
SWEET
PICKLES
CAIN'S
PICCALILLI
FORMAN'S
ACUUM" SEALING

less than 10 per cent annually. Sometimes wheat germ oil is added as an anti-oxidant; this oil is rich in vitamin E, but the amount present in a small capsule hardly warrants the claim that it contains vitamin E. Although we have no recognized units of vitamin E and we do not know the human requirements of this vitamin, it is given in doses of 3 to 5 grams or more in therapeutic cases.

A solution of the vitamins A, B_1, B_2, C, and D in 80 per cent alcohol is said by a pharmaceutical house which prepares such a product, to be stable. It is not stated what the other 20 per cent of the solvent is, but it can be assumed that it is not water.

It is common practice to impart an excess, beyond what is claimed on the label, to products containing easily destroyed vitamins, such as vitamin A. A certain highly concentrated vitamin A oil which is sold to manufacturers and claimed to contain 200,000 units per gram actually contains 210,000 units per gram.

We shall now consider the stability of the individual important vitamins of commerce:

Vitamin A— Vitamin A is slowly destroyed by exposure to the air and light. Even in fish oil, which is our most important source of vitamin A, this destruction is material. To prevent, or at least reduce it, some of the commercial producers of fish-oil concentrate now store the oil in barrels in which they introduce carbon dioxide gas in order to exclude air as far as possible. Strangely enough, carbon dioxide is quite soluble in these oils.

Vitamin A is also destroyed by the enzymes lipase and lipoxidase (which are found in the livers and split oils and fats to form free fatty acids). Therefore, some fish oils which are produced by autolysis (i.e., by letting the fish liver decompose in the sun until the oil cells are so tender that the oil can be pressed out—resulting in exposure to this enzyme action) frequently are completely void of the vitamin. These active enzymes can also be produced by some micro-organisms. Some feeds contain enzymes which are able to destroy vitamin A (carotene) when fed in the same ration. These enzymes may be present in dried milk, fish and meat products. In some cases these enzymes are active in the dry state. Heating will in many cases destroy or inhibit such enzymes. Many metals, such as iron, copper and zinc, have a pro-oxidative action and should therefore not be allowed in contact with vitamin-A oil.[1]

All light of wave lengths shorter than 5000 A. U. should be eliminated from vitamin products. Some red cellophanes are very efficient filters for the removal of such undesirable light.

Fortunately, there are available many preserving agents which frequently are quite effective; some of them are able to postpone oxidation for several years. Partial hydrogenation[2] has been tried and is said to be quite effective. The addition of anti-oxidants is the most common procedure. Such agents may be extracted from various seeds. Carrot and soy bean seeds are particularly good.[3] Oat flour and soy bean flour are frequently used and have been the subject of many patents. Wheat-germ oil, which is our best commercial source of vitamin E, is also commonly used. Some resins from plants are effective under certain conditions and have been reported to be satisfactory in some manufactured products. Among the chemical anti-oxidants hydroquinone, catechol, pyrogallol and hydroxyhydroquinone are used to some extent.[4]

In considering any anti-oxidant it will be wise to check the toxicity of the finished product. From a chemical aspect an anti-oxidant is apparently just an agent which is oxidized easier than the vitamin, and the anti-oxidant consequently absorbs the oxygen which comes in contact with the product before the oxygen is able to affect the vitamin. The action therefore provides only a temporary postponement of the vitamin destruction—this postponement, however, may be for a period of several years.

Complete exclusion of air, whenever possible, is preferable. Medical tablets have been made, consisting of fish-oil concentrate absorbed by an inert powder and subsequently pressed into tablets and coated with several layers of sugar. Such tablets have been found satisfactory after several years of storage under ordinary conditions.

These oxidation processes are greatly accelerated by temperature. As a result, *it is always advisable to store*

(Continued on page 307)

VITAMINS ON THE DINING TABLE. *Increasing interest in supplementing the diet with a daily ration of the B-complex vitamins has been stimulated by the latest discoveries in the vitamin field. Among the many forms and combinations in which this can be taken is B-Nutron Syrup, a high-potency source of the entire complex, obtained from rice bran concentrates and supplemented with synthetic thiamin* (B_1), *riboflavin* (B_2), *and nicotinic acid, plus iron in the form of the gluconate (non-toxic). Produced by the Nion Corporation, Los Angeles, it comes in 4-, 8-, and 16-oz. bottles, and a 2-oz. dropper bottle with carton (Angelus Paper Box Co.). Package design and container by Owens-Illinois.*

Wide-mouth glass containers are approved by pharmaceutical houses packing vitamin capsules, because capsules in glass keep dry and firm and the wide mouth is superior from a packaging standpoint. These high-potency Vitamin A B G D Concentrate Capsules are produced by Frederick Stearns & Co. of Detroit (one of the earliest concentrate-tablet makers). Round Owens-Illinois jars, holding 25, 100, *and* 250 *capsules,*

Ronald ✓
Dougherty ✓
Harry

How to reduce the instability of vitamin content

(*Second article of a series on techniques of vitamin fortification*)

By **HALFDAN HEBO, D.Sc., F.R.N.S.**, New York[*]

> The manufacturer who has considered the question, "Shall we add vitamins to our products?," (subject of the first article in this series) is confronted immediately with a further consideration. This is the matter of vitamin-content retention in the products to be fortified. Dr. Hebo now takes up the use of special processing techniques and the addition of preserving agents to accomplish satisfactory retention.—The Editor.

One of the most difficult phases of food processing is the problem of proper retention of vitamins, whether they be naturally present or added. Vitamin D is the only one which is reasonably stable during ordinary processing and long-period storage conditions. Fortunately, a study of vitamin chemistry provides us with some inside knowledge of conditions which destroy the various vitamins. By avoiding certain conditions in processing, such as high temperatures and oxygen, we are frequently able to prevent material destruction of these vital components.

Vitamins have only one thing in common: their names. Now that the tendency is to call them all by their chemical names, rather than by their letters, it is safe to state that they have really nothing in common. They are not in every case necessary for human nutrition. For example, vitamins B_3, B_4, B_5 are not required by man; and apparently vitamins L_1 or L_2, which support lactation, may be dispensed with even during lactation if certain other food factors are present. Other food factors which are definitely essential for sustaining human life are not known as "Vitamins." Calcium, phosphate, iron, iodine, and amino acids are but a few of several dozen chemicals which we must have in our daily diet to live.

While most of these other essential food factors have fairly simple molecules, some of the vitamins have large intricate chemical formulae. For instance, the vitamin D (calciferol) molecule consists of 70 atoms; vitamin A has 51 atoms; B_1, 38; and C, 20 atoms.

It is quite reasonable to suspect that some of these chemicals may react chemically with each other and form new, inactive compounds. There has even been some talk of "Anti-vitamins"—if we were to accept this term, *oxygen* ought to rank first among these "fifth-columnists" of biology, because all of our known vitamins succumb to its merciless attack. Some enzymes are likewise enemies of the frail vitamins and a number of metals and metallic salts destroy or counteract the vitamins. Ultra-violet rays, which are used in creating the D vitamins, destroy all the vitamins including those which are created by it, if exposure to the rays is prolonged sufficiently.

A typical example of vitamin conservation and destruction in various methods of food preservation has recently been reported by Farrel and Fellers.[11] They preserved beans by canning, quick-freezing and dehydration. The Bountiful variety of snap beans were quick-frozen and were blanched (scalded) before freezing. The following table indicates the vitamin content before and after processing. After one year of storage the vitamin losses were reported to be negligible.

	Fresh raw beans.	Canned	Quick-frozen	Dehydrated
Vitamin B_1 (International units)	16	14	19	20
Vitamin B_2[*] (Bourquin-Sherman units)	33	32	39	40
Vitamin C (International units)	400	64	218	18

The blanching process as a preliminary treatment to canning or freezing appears to be of utmost importance in conserving vitamins B_1 and C because it inhibits or destroys some of the destructive enzymes which frequently are present in vegetables, fruits and oils. In this experiment vitamins B_1 and B_2 were tested biologically on rats. The apparent increase of these two vitamins in quick-freezing and dehydrating may be credited to the enzyme-inhibiting treatment (blanching). It appears that these enzymes, if not inhibited or destroyed, are active and may destroy the vitamins *after* the beans have been consumed by the test animal.

After canning and processing of foods, it is frequently observed that the water-soluble vitamins are present in the liquid rather than solid part of the product. In such cases the consumer should be advised to use the entire content of the package.

A concentrated mixture of all the vitamins is surprisingly stable if no water is present. Such a mixture, consisting of shark-liver oil containing in excess of 100,000 units of vitamin A per gram, mixed with crystalline vitamin B_1, B_2 and C, with vitamin D concentrate added, is used for capsulating and has been found satisfactory. The deterioration under normal conditions is frequently

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[*] Dr. Hebo received a degree in Chemical Engineering from the Royal Polytechnical Institute, University of Copenhagen; and is a Fellow of the Royal Nordic Society at Copenhagen, oldest scientific society in the world. In the last ten years he has specialized in the chemistry of ultra-violet irradiation, as applied to vitamin-content of food and dairy products and in connection with the measurement of vitamin-content by spectroscopy. In 1934, he introduced the Titus Lamp for treatment of erysipelas. Dr. Hebo has been retained in a consultative capacity by leading American food and pharmaceutical concerns.

[*] A Bourquin-Sherman unit of vitamin B_2 is the amount of the vitamin necessary to produce a specified amount of growth in rats. It cannot be translated directly into weight units and various investigators have reported it equal to from 2 to 7 micrograms.

How to reduce instability of vitamin content

(Continued from page 286)

vitamin-A concentrates and products at as low temperatures as possible and practical.

Vitamin B_1—Vitamin B_1 is more stable to oxygen than vitamin A; but is is easily destroyed by mild reduction agents, such as sulphites and tannins, by permanganates, tartrates and manganese oxide; and by hot alkalies. The vitamin in an acid medium is fairly heat-stable and will stand ordinary processing with a minimum loss. For instance, tomato juice heated to 100° C. for four hours with a pH adjusted to 4.28, lost only 20 per cent of its vitamin B_1 content, but with an adjusted pH of 5.2 the loss was 30 per cent and at a pH of 7.9 the loss was 70 per cent.[5]

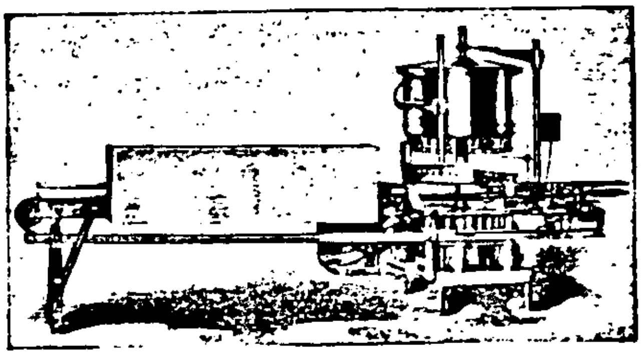
A weak solution of the vitamin in plain water is not stable and some of the commercial products thus sold, particularly those sold for stimulating plants, have in many cases been found to be deficient in B_1. It appears that the stability of the vitamin naturally found in common foods is greater than in pure form; this has been attributed to a chemical combination it forms with pyrophosphoric acid. In general, it can be stated, it is not necessary to add a preservative agent to foods containing or enriched with vitamin B_1. Even by baking only 5-9 per cent is lost in potency, although in toasting whole-wheat bread as high as 17 per cent sometimes is lost. The best way to preserve the vitamin is to lower the pH concentration of the product whenever possible.

Other B Vitamins—Riboflavin or B_2 is, like vitamin B_1, fairly stable but subject to destruction by reduction. It is stable at higher temperatures and decomposes first at 274° C; but it is readily destroyed in alkali solution, particularly if exposed to strong light, visible as well as ultra-violet. In food processing no noteworthy loss of the vitamin is observed. Due to its relatively high cost thus far, it is infrequently added to food products.

Nicotinic acid, which recently entered the vitamin kingdom, is one of the cheapest vitamins, and is already being added commercially to flour. It is even stable above 230° C, which is its boiling point, so in this respect no precautions are apparently needed.

Vitamin C—Vitamin C is one of the frailest of the vitamins: oxidation, alkali, metals, heat, and ultra-violet light are among its many enemies. The best way of preserving the vitamins is to exclude as many of these destructive elements as possible. At low temperatures in an acid medium, oxidation is insignificant, but at prolonged heating the destruction is rapid. Frozen orange juice loses little of its vitamin-C content during a year of storage, and flash pasteurization in vacuum does not affect the vitamin content materially. Metals, particularly copper and iron, should be carefully excluded from contact with foods containing Vitamin C. A little speck of rust quickly oxidizes the vitamin. Riboflavin in aqueous solution will also inactivate it, particularly if exposed to light. The dry crystal is remarkably stable and will stand exposure to air for years without being destroyed by oxidation.

Ordinary processing destroys about 50-85 per cent of the vitamin C content of foods, but it has been reported that the addition of common salt (sodium chloride) to vegetables in some cases acts as a preservative of the vita-



min, perhaps because this addition makes oxygen less soluble in the water in which the vegetables are cooked. Many of the enzymes ordinarily found in fruits and vegetables are supposed to be responsible for a material part of the destruction; such losses can be reduced if the foods are placed in boiling water instead of beginning the cooking in cold water[6] Processing in vacuum also will reduce the loss considerably. It has been reported that it is possible to can tomato juice without loss of vitamin C at all.[7]

When fruits and vegetables are crushed, enzymes are liberated. This leads to substantial vitamin destruction. In some cases this can be prevented by inactivation of these enzymes by quick-heating before crushing. Processing at low-pH concentration preserves the vitamin-C potency and the canned citrus juices may contain 70-90 per cent of their original vitamin-C content.

Vitamin D—Chemically, vitamins D_2 and D_3 are so much alike that here they will be dealt with jointly as just "vitamin D." This D can be regarded as one of the most powerful of the vitamins: one ounce of it will cure 40,000,000 rickety rats. It is also one of the most stable vitamins. Under ordinary conditions it will withstand oxidation, heat, and ordinary light—although short ultraviolet rays will destroy its antirachitic power and will under certain conditions form a toxic compound: toxisterol. The vitamin is fat-soluble and it is reported that it is more active if it is dissolved in a non-saturated fat, such as a fish oil.[8]

It might be mentioned in passing that a few years ago it was reported that cereals were rachitogenic (i.e., ricket-creating) and this was blamed on a substance known as phytin. This factor was also called "toxamin" by the American Medical Association's Council on Foods (1937).[9] Others have reported that beryllium[10] and its salts were rachitogenic. These are the two major factors which affect the calcium-phosphate metabolism despite the presence of a normal supply of vitamin D.

The food-packing industry should not be concerned about these rachitogenic factors at the present time. Beryllium is infrequently found in foods. The phytin problem has not been defined and authorities disagree as to its importance. But it should be pointed out that vitamin D is ineffective *unless the body is adequately supplied with calcium and phosphate salts in a form in which they may be assimilated.* It is therefore advisable to add these salts to food products which have been enriched with vitamin D, when it is practicable and possible to do so. The human body requires a minimum of about one and a half grams of calcium and one gram of phosphorous daily.

This vitamin is destroyed after prolonged heating at 200° C, even if air is excluded.

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[9] Jnl. Amer. Med. Ass., v. 109, p. 30.
[10] Guyatt, Kay & Branion, Jnl. Nutr., v. 6, p. 313, 1933.
[11] Kenneth T. Farrell & Carl Fellers: 101st Meeting Amer-

65-4307

Ex 120

Guacama soln ( )

Discussion: 1, only 38% of the total alkali
~~has~~ ~~[illegible]~~, here
(as carbonate) is present as HCO_3; as compared
to 73% for 2 and 81% for 3. At the end
only 16% of the available CO_2 has been
evolved (the carbonate content is 32%). and
the water adapted has reached. The
the water [illegible] an
amazing figure of 37 gms/gm CO_2 as
the soln did not boil at 100°C it is
~~[illegible]~~ likely that the evolu. of CO_2 would
be far ~~[illegible]~~ increased at a higher temp.
but how much greater would the
the increase in solns. 2 & 3 at these
temps?

900% greater than 2 & 1000% greater
than 3;

64% the available
2: The CO_2 evolved is 850% greater
than 1. The soln is clear after
only forty min & at this point
the water evolved is only 1.4 gms
/gm CO_2. Would it be worth
while to stop the ~~[illegible]~~ decomp. at this
point? The ~~same~~ puzzling slowing
down in the last 80 ~~min~~ may ~~[illegible]~~ very
3: likely be due to the action of the alkali
on the oily packing as an increase

Expt C4.3

CO2 Recovery

Problem: To detn ~~the~~ on a comp. basis the rates of decompn. of [illegible]

1. Soln

2. Soln $\left\{ \begin{array}{l} Na_2CO_3 \\ NaHCO_3 \end{array} \right.$ + 25 g NaHCO3 freshly pptd.

3. Soln $\left\{ \begin{array}{l} Na_2CO_3 \\ NaHCO_3 \end{array} \right.$ + 35 g NaHCO3 freshly pptd

at 100 °C

Summary: The rate of decompn. & evapn of H_2O was detd. in the cases [illegible] 3 & 4 the results agree very well of [illegible] instead of expt. [illegible] for the first two [illegible] & the evoln. of CO2 is somewhat slowed down expt. for 2. This may very likely be due to the action of the alkali on the new packing which was considerable & was dissolved into the soln.

Procedure: used 8" steam coil & 10 °C in steam [illegible]

CO2	Heating per CO2
105° - 1 hr. = 40 grs.	4.2 lbs
110° - 1 hr = 60 "	6 "

(125 cc) 60 grs suspension
6.7 grs Na_2CO_3 in sol.
10.0 $NaHCO_3$
76.7 grs. { 6.7 grs Na_2CO_3. / 71. grs $NaHCO_3$. = 18.5 grs CO_2.

120 cc = 60 min = 3.5 grs CO_2.

20% CO_2 -
25% in sol
85% more to decompose

6.7 grs Na_2CO_3
8.5
15.2 grs Na_2CO_3

This info. is necessary to ~~[illegible]~~ ~~[illegible]~~ ~~[illegible]~~ obtain a heat balance which in turn determines the form & size of the apparatus & the amount of decomposition

1/1/50

Note on ClO₂ Research 10 # 2 9/28/47

Data for a 1 Ton Plant

The information we have obtained so far is more qualitative than quantitative due to ~~various~~ number of uncontrollable variable factors in the expts. The following ~~data~~ points ~~should~~ must be ~~a~~ detailed

1\. ~~Data~~ a ~~on~~ very careful ~~on~~ carbonation run using

a. 25 gms NaClO₂ / 100 gms H₂O

b. ~~[illegible]~~ a gas flow of 900 c.f.p.h. ~~[illegible]~~

c. a carbonation temp of ~~[illegible]~~ -18°C.

From this ~~The~~ point to which it is feasible ~~[illegible]~~ to carry the carbonation should be very carefully ~~found~~ ~~[illegible]~~ as this point ~~determines~~ fixes both the amount of carbonation and the composition of the dissociation mixture. This part is more fully discussed in note # 1.

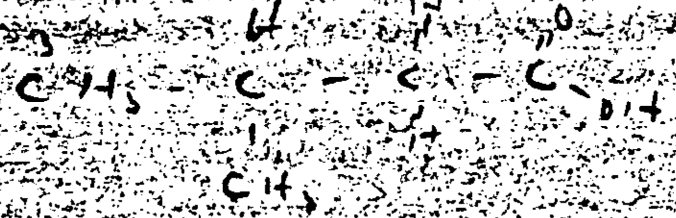
2\. Decomposition Data at 100°, 105, and 110°C using 25 and

acids

Gen Formula $C_nH_{2n}O_2$ $\quad -C\overset{O}{\underset{OH}{\diagdown}}$ carboxyl

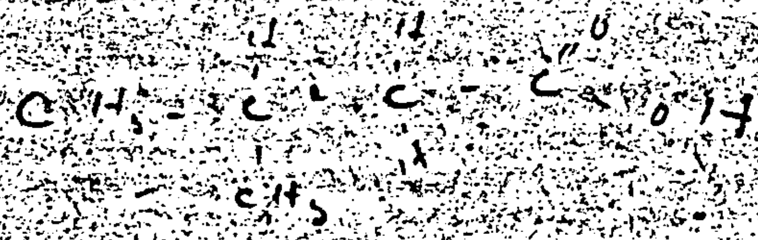
nomenclature

1. Geneva



$CH_3-\underset{CH_3}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-C\overset{O}{\underset{OH}{\diagdown}}$ 3-methyl butanoic acid

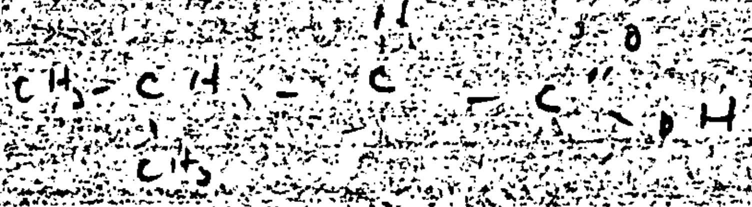
2. carboxylic acid



$CH_3-\underset{CH_3}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-C\overset{O}{\underset{OH}{\diagdown}}$

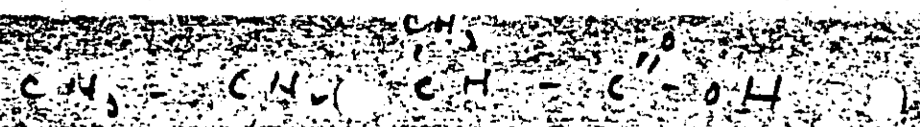
2-methyl-1-propanecarboxylic acid

3. acetic acid derivative



$CH_3-\underset{CH_3}{CH}-\overset{H}{C}-C\overset{O}{\underset{OH}{\diagdown}}$ isopropyl acetic acid

4. formic 1	lauric 12
acetic 2	myristic 14
propionic 3	palmitic 16
n-butyric	stearic 18
valeric	
caproic $CH_3-(CH_2)_4-C\overset{O}{\diagdown}OH$ 6	

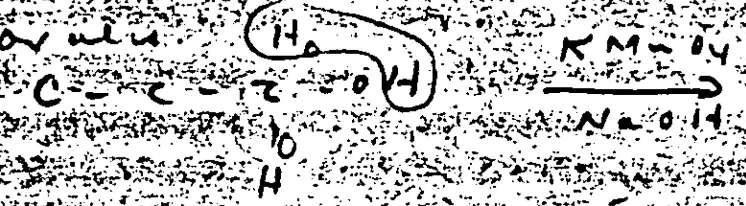


$CH_3-CH_2-\overset{CH_3}{CH}-\overset{O}{\overset{\|}{C}}-OH$

α- methyl butyric acid

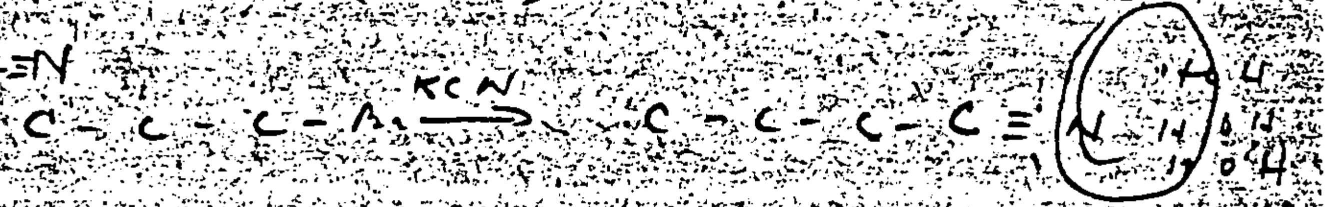
Synthesis

1. oxidation

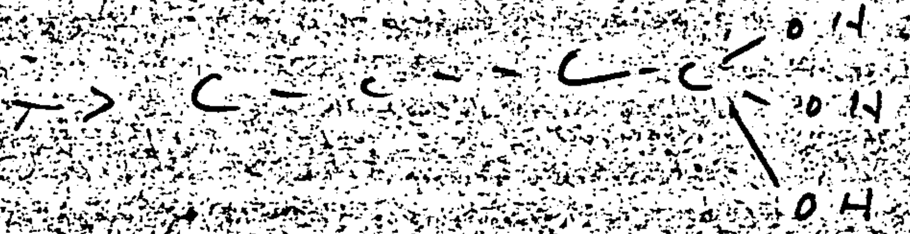


$C-C-\underset{OH}{\overset{H_2}{C}}-OH \xrightarrow[NaOH]{KMnO_4}$

2. —C≡N

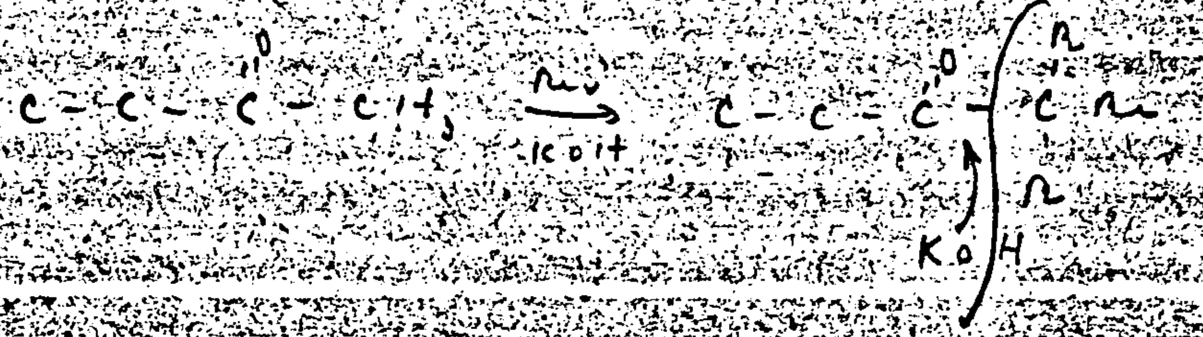


$C-C-C-Br \xrightarrow{KCN} C-C-C-C\equiv N \quad H\text{-}OH \quad H\text{-}OH \quad H\text{-}OH$



$\rightarrow C-C-C-C\begin{matrix}OH\\OH\\OH\end{matrix}$

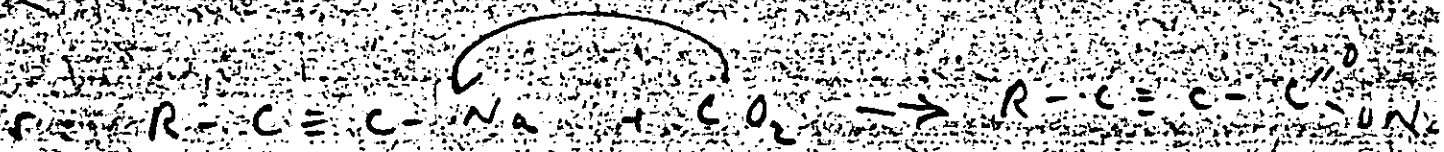
3.



$C-C-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[KOH]{Br_2} C-C-\overset{O}{\overset{\|}{C}}-\overset{Br}{\underset{Br}{C}}Br \quad KOH$

4. $KMnO_4 \xrightarrow{\Delta}$

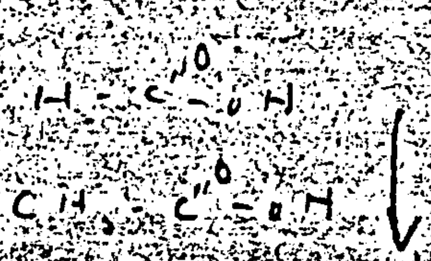
5.



$R-C\equiv C-Na + CO_2 \rightarrow R-C\equiv C-\overset{O}{\overset{\|}{C}}-ONa$

Reactions

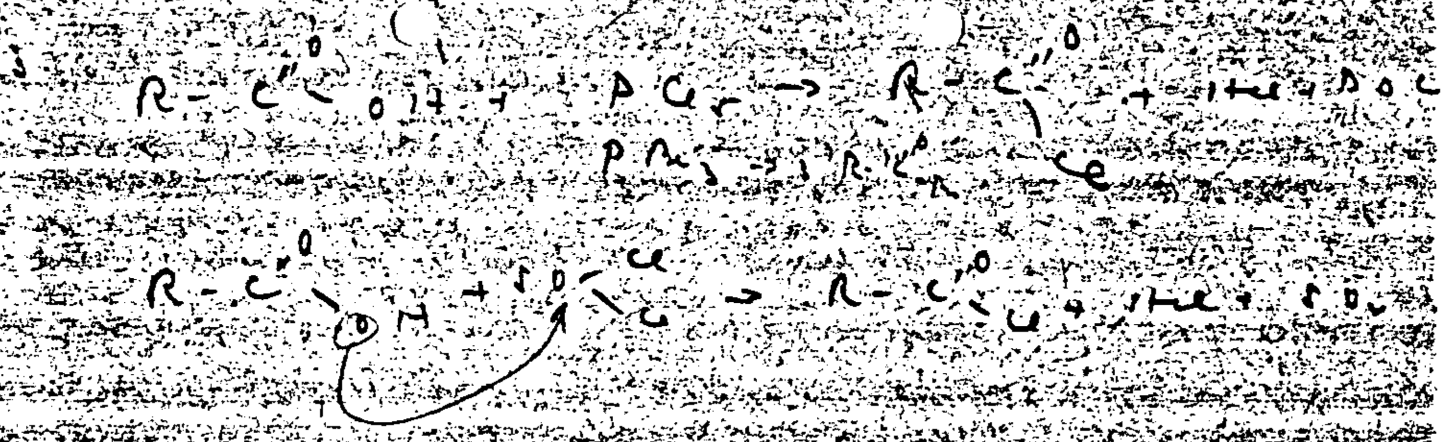
1. Ionization



$H-\overset{O}{\overset{\|}{C}}-OH$

$CH_3-\overset{O}{\overset{\|}{C}}-OH$

[illegible]

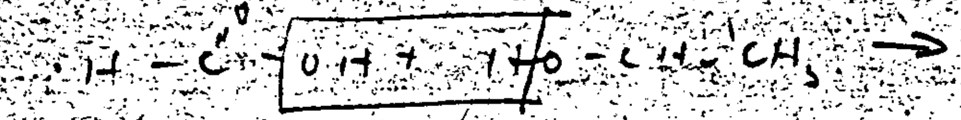


$R-C(=O)OH + PCl_5 \rightarrow R-C(=O)Cl + HCl + POCl_3$

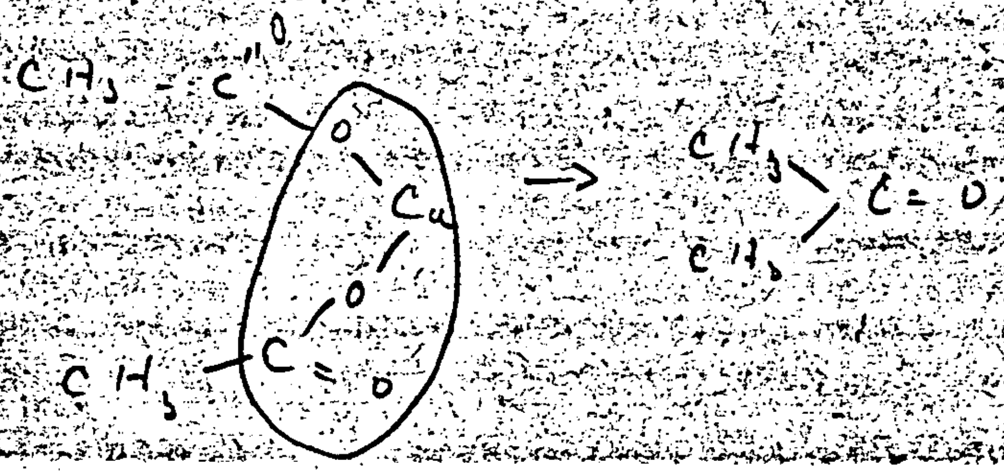
$PCl_3 \rightarrow R-C(=O)Cl$

$R-C(=O)OH + SOCl_2 \rightarrow R-C(=O)Cl + HCl + SO_2$

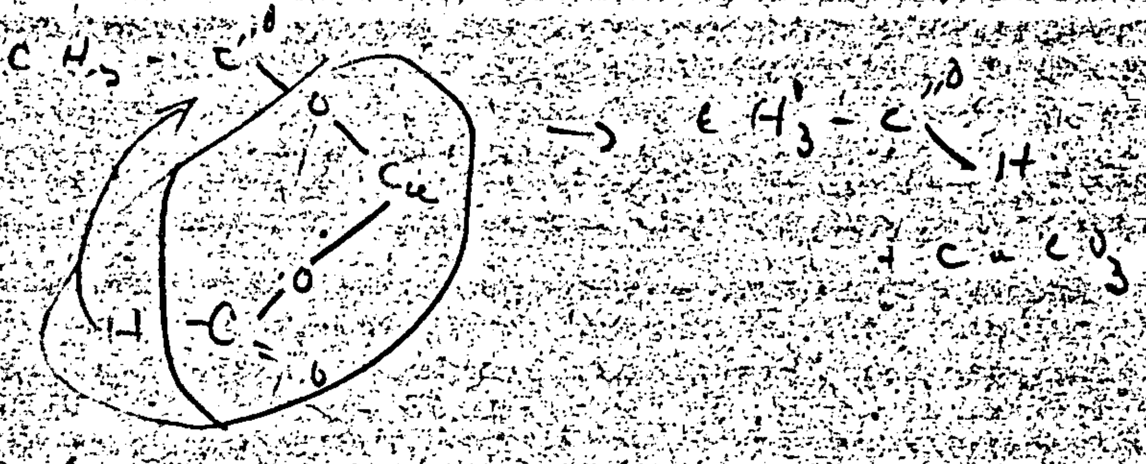
4. Esters



$H-C(=O)-\boxed{OH + H}O-CH_2-CH_3 \rightarrow$

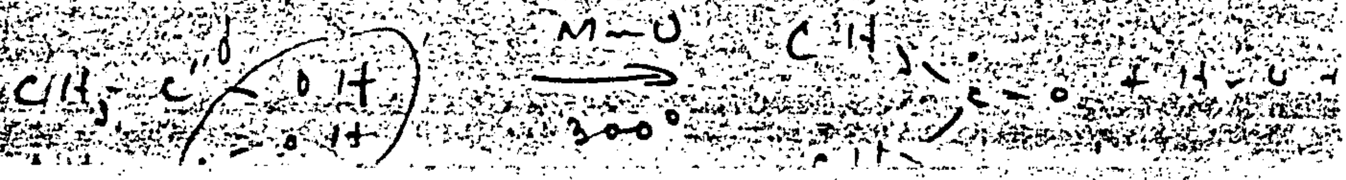


$\rightarrow (CH_3)_2C=O$



$\rightarrow CH_3-C(=O)H + CuCO_3$

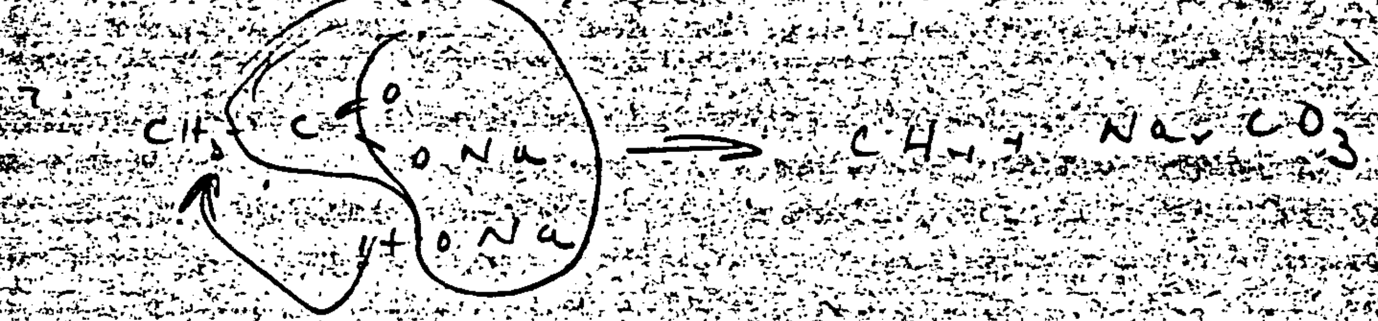
also can



$CH_3-C(=O)OH \xrightarrow[300°]{MnO} (CH_3)_2C=O + H-O-H$

6. Cannot oxidize, reduce, or dehydrate
can reduce if

$CH_3-\overset{O}{\overset{\|}{C}}-Cl + H_2 \xrightarrow{Pd}$



7. $CH_3-\overset{O}{\overset{\|}{C}}-ONa + H-ONa \rightarrow CH_4 + Na_2CO_3$

Special

1. Stepping-up series

$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{PCl} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-Cl$

$\rightarrow CH_3-CH_2-\overset{H}{\underset{H}{C}}-OH \xrightarrow{PBr_3} CH_3-CH_2-CH_2$

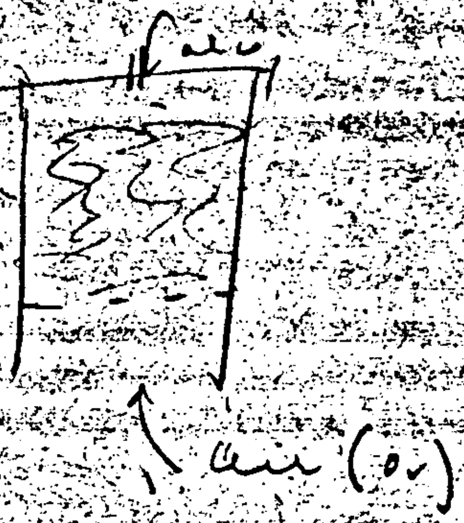
$\xrightarrow[H_2O]{KCN} CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH$

2. Separation of acids
(a) make methyl ester with CH_3-OH
(b) Fractional [illegible]

Individual acids

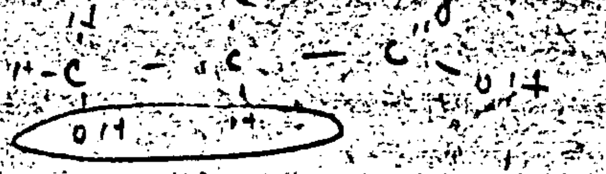
1. Formic
$C=O + NaOH \rightarrow H-\overset{O}{\overset{\|}{C}}-ONa$

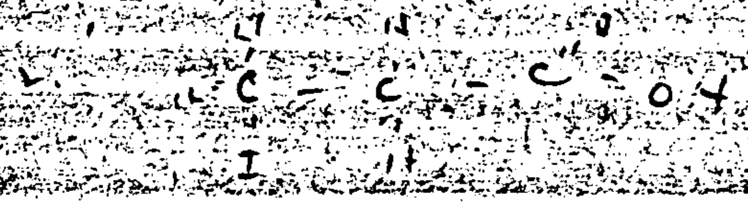
Acetic Acid



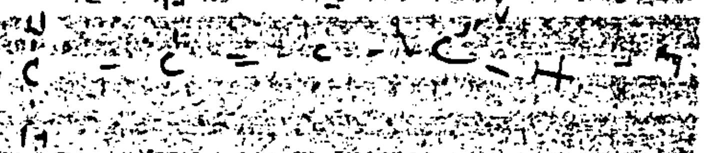
Unsat. Acids

Prep

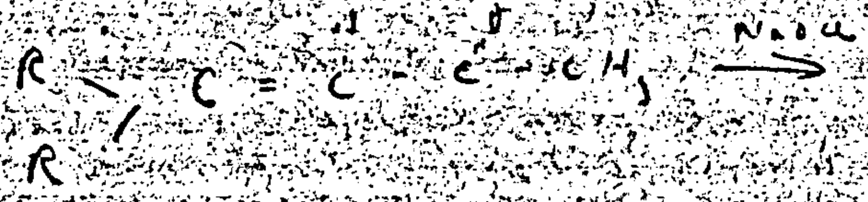




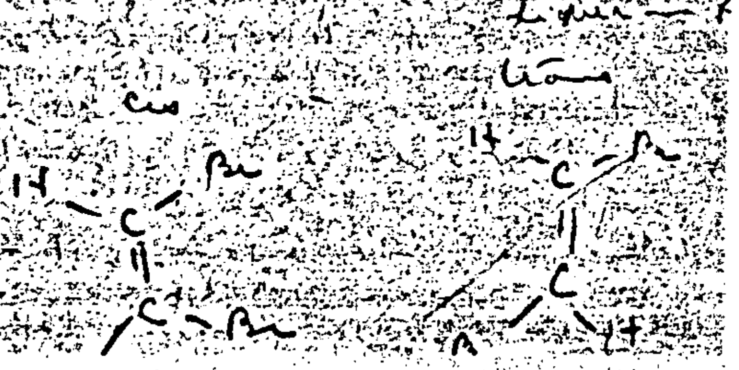
3) aldol cond. →



4)



Isomerism (Geo)



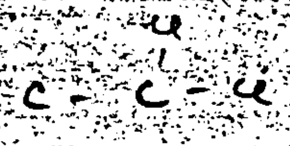
Classes < mono-halogen ( )
polyhalogen

nomenclature (mono)

alkyl radical + halogen

C-C-C-Cl - n-propyl chloride

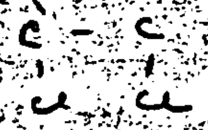
Poly-



$C-C(Cl)_2$

geminal

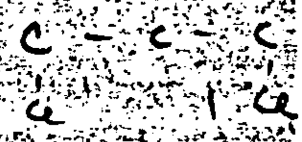
ethylidene chloride



$ClC-CCl$

vicinal

ethylene chloride



$C(Cl)-C-C(Cl)$

separated dispersed

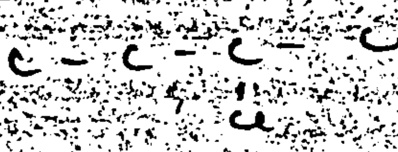
Cl-C-C-C-C-Cl

α,δ-dichlorobutane

Synthesis (mono)

1. alcohol + PCl_5 [$SOCl_2$, PCl_3, HCl ($ZnCl_2$)]

$C-C-C-OH + PCl_5 \rightarrow C-C-C-Cl + POCl_3 + HCl$

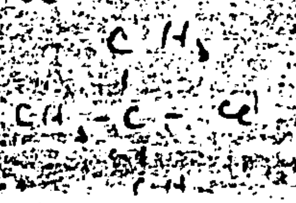


For $C-C-C(Cl)-C$ use C-C-C=C

Cl·H

Mk rule

HI too good



For $CH_3-C(CH_3)-Cl$ from corr. alc., goes on fairly easily.

[illegible]

1. $CH_3-CH_2-\overset{O}{C}-H + PCl_5 \rightarrow CH_3-CH_2-\overset{Cl}{\underset{H}{C}}-Cl + POCl_3$

or $CH_3-\overset{O}{C}-CH_3 \xrightarrow{PCl_5} CH_3-\overset{Cl}{\underset{Cl}{C}}-CH_3$

can put on Br but not I.

Vicinal

$C=C + Cl_2 \rightarrow \underset{Cl}{C}-\underset{Cl}{C}$

gem.

(a) $H-C\equiv C-H + HBr \rightarrow H-\underset{H}{C}=\underset{Br}{C}-H \rightarrow H-\overset{H}{\underset{H}{C}}-\overset{Br}{\underset{Br}{C}}$

(b) $-\underset{|}{C}-\overset{O}{C}-H + PCl_5 \rightarrow -\underset{|}{C}-\overset{Cl}{\underset{H}{C}}-Cl$

Special Cpds

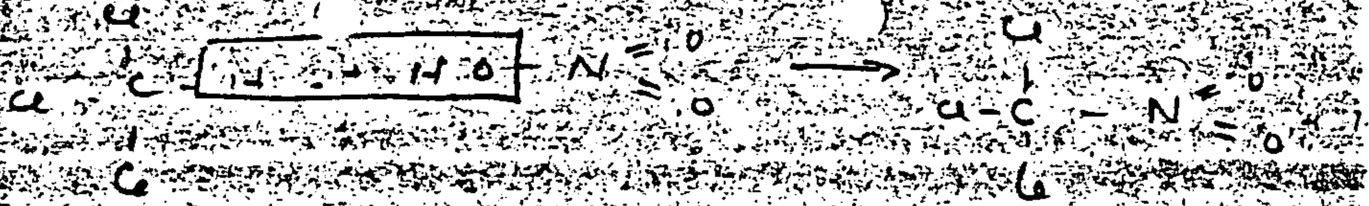
$C-Cl_4$ importance:
- solvent
- prep $CHCl_3$
- fire [illegible]
- medicinal prep.

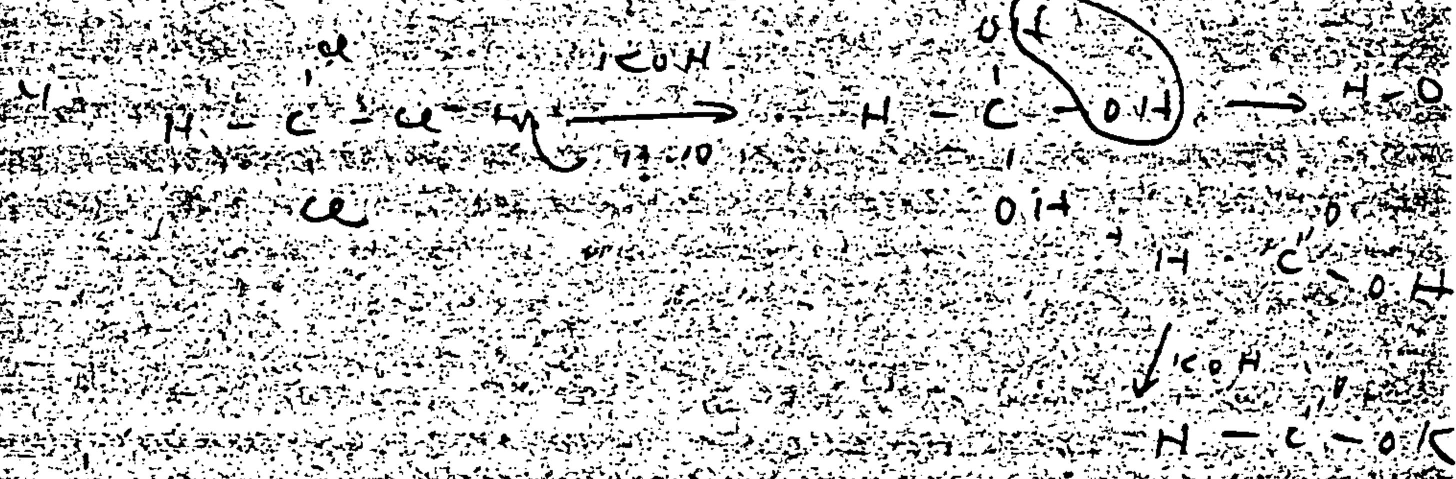
Prep. $CH_4 + 4Cl_2 \rightarrow CCl_4 + 4HCl$

$C + 2S \xrightarrow[\text{furn}]{\text{elec}} CS_2$

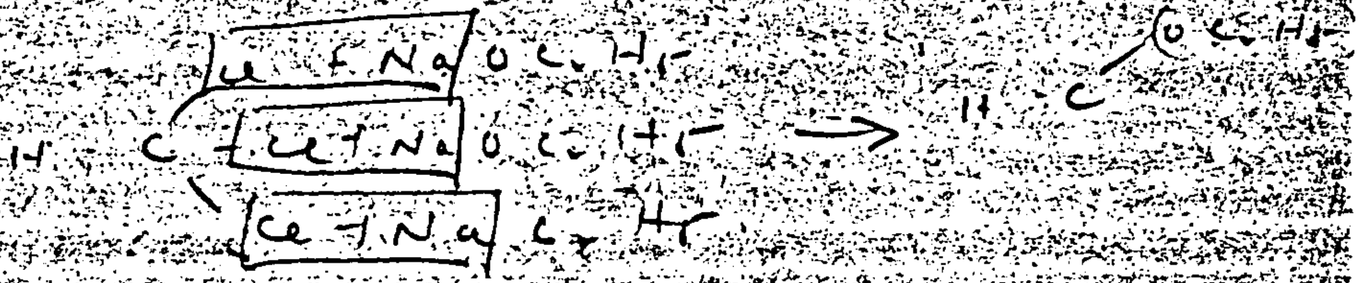
$CS_2 + 3Cl_2 \rightarrow Cl_3-C-Cl + S_2Cl_2$

chloropicrin

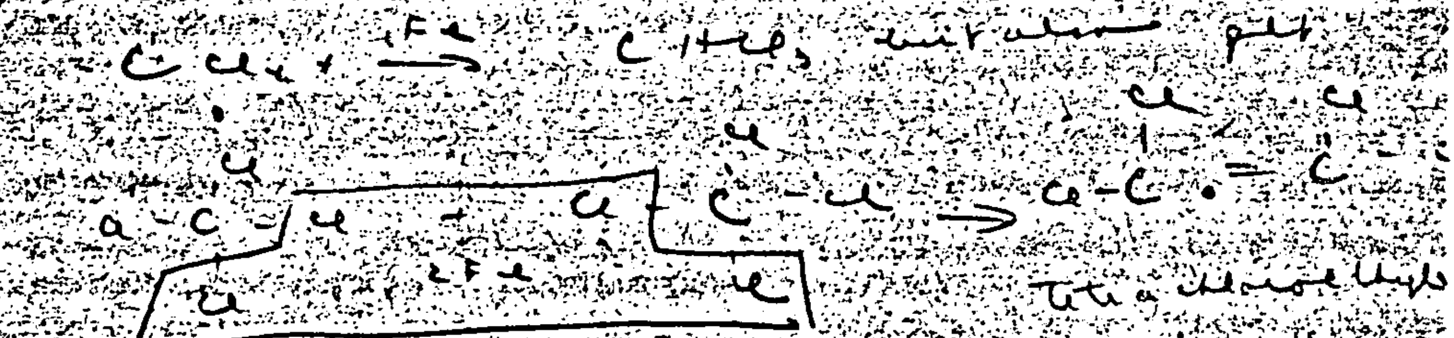




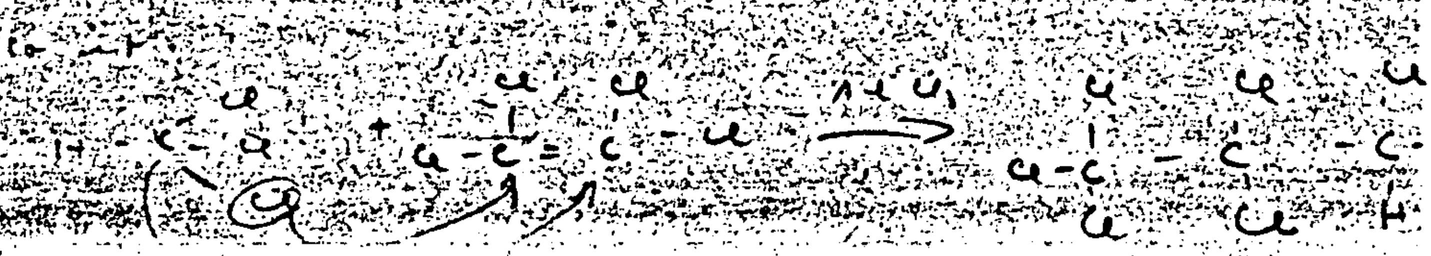
Ethyl ortho formate



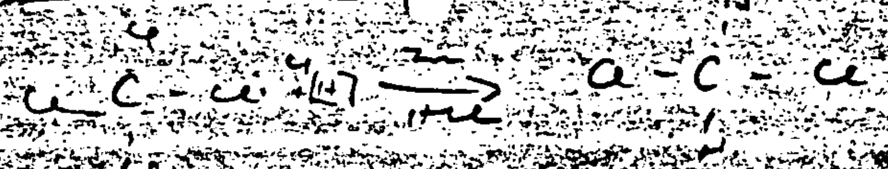
addition Reactions



Tetrachloroethylene



Reduction

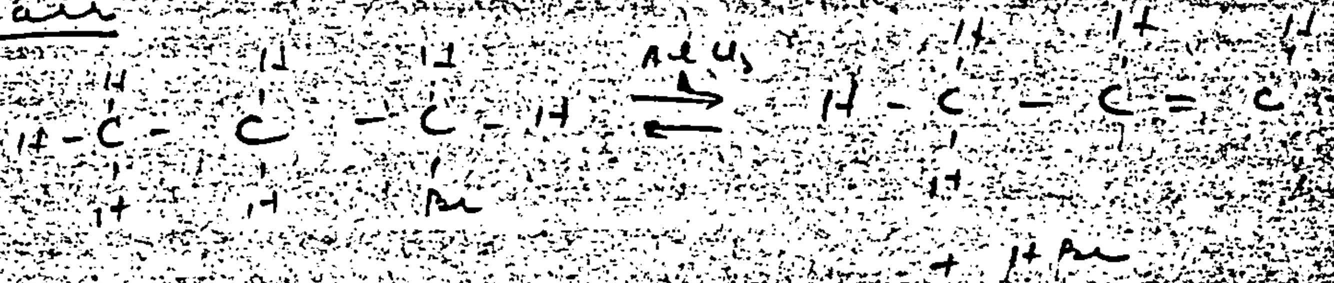


$$Cl-\overset{Cl}{\underset{Cl}{C}}-Cl + [H] \xrightarrow[HCl]{Zn} Cl-\overset{H}{\underset{H}{C}}-Cl$$

methylene chloride

but CH_3I much more [illegible]

Rearr

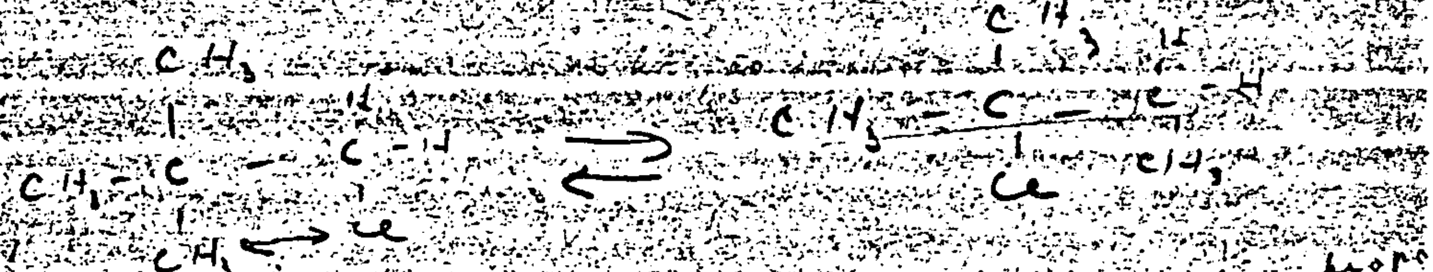


$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{Br}{C}}-H \overset{AlCl_3}{\rightleftharpoons} H-\overset{H}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{C}-H + HBr$$

acc. to [illegible] rule

$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{Br}{C}}-\overset{H}{\underset{H}{C}}-H$$

also



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{H}{C}-H \rightleftharpoons CH_3-\overset{CH_3}{\underset{Cl}{C}}-\overset{H}{C}-H$$

2 methyl 2 chloro prop

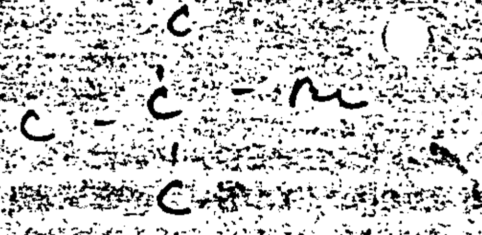
Reactivity

Rate depends on length of R

CH_3-Br

CH_3-CH_2-Br ↓

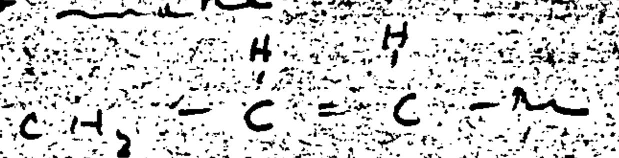
also,



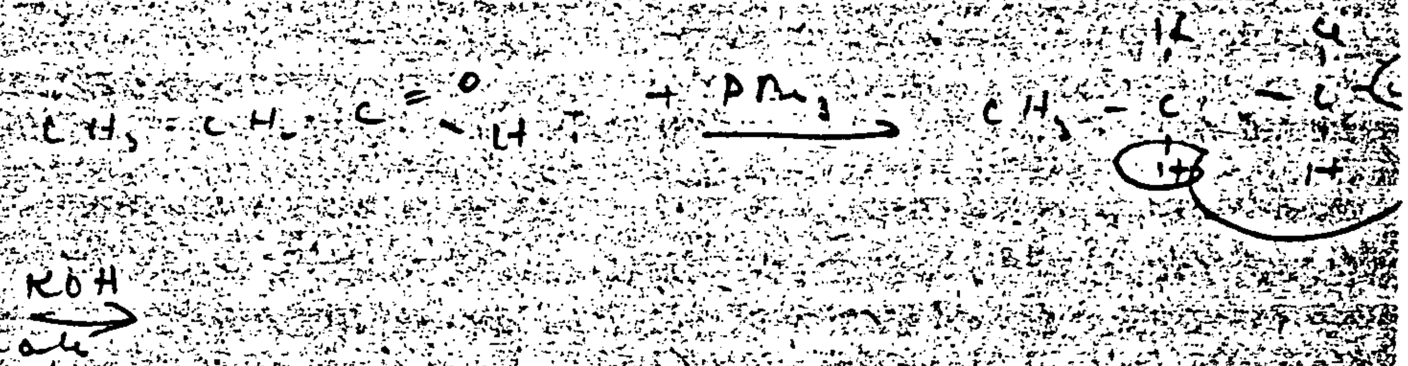
$C-\overset{C}{\underset{C}{C}}-Br$ very inactive as is

$C-C=C-Br$

How make



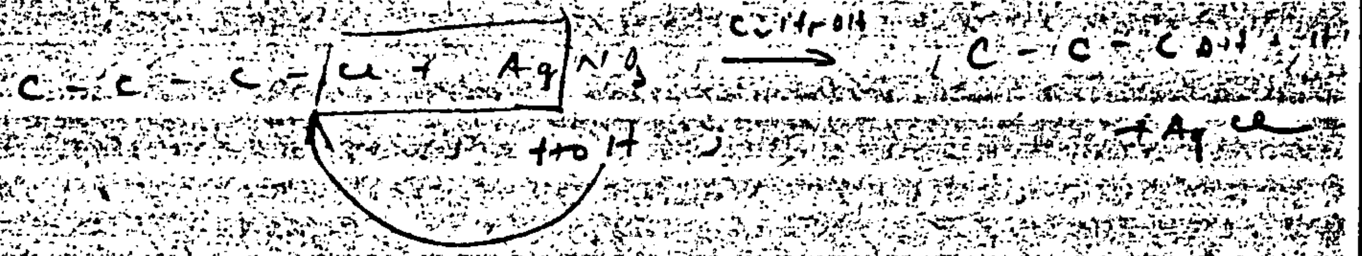
$CH_2-\overset{H}{C}=\overset{H}{C}-Br$? (



$CH_3-CH_2-C{=O \atop -H} + PBr_3 \longrightarrow CH_3-\overset{H}{\underset{H}{C}}-\overset{Br}{\underset{H}{C}}-Br$

$\xrightarrow[alc]{KOH}$

Test for active Halogen



$C-C-C-\boxed{Cl + Ag}NO_3 \xrightarrow{C_2H_5OH} C-C-C\,OH + H$

$+ HOH$

$+ AgCl$

Cyanides and nitro Cpds

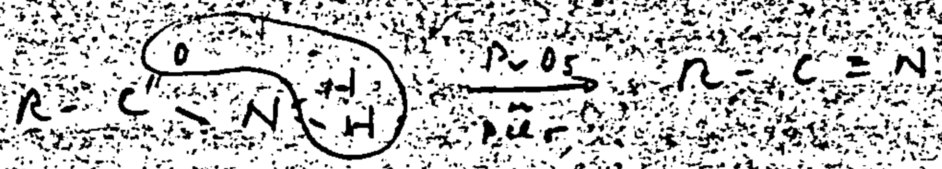
Nomenclature

HCN hydrogen cyanide formonitrile
formic nitrile

CH_3-CN methyl cyanide aceto nitrile

Preparation

1. Dehydration of an amide

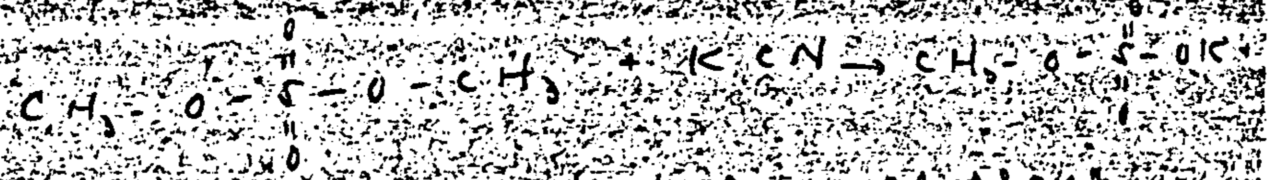


$$R-\overset{O}{\overset{\|}{C}}-N\begin{matrix}H\\H\end{matrix} \xrightarrow[\text{heat}]{P_2O_5} R-C\equiv N$$

2. alkyl halide + KCN

$$R-I + K-CN \rightarrow R-C\equiv N + KI$$

3. for ethyl and methyl cyanides the cheaper alkyl sulfates are used.

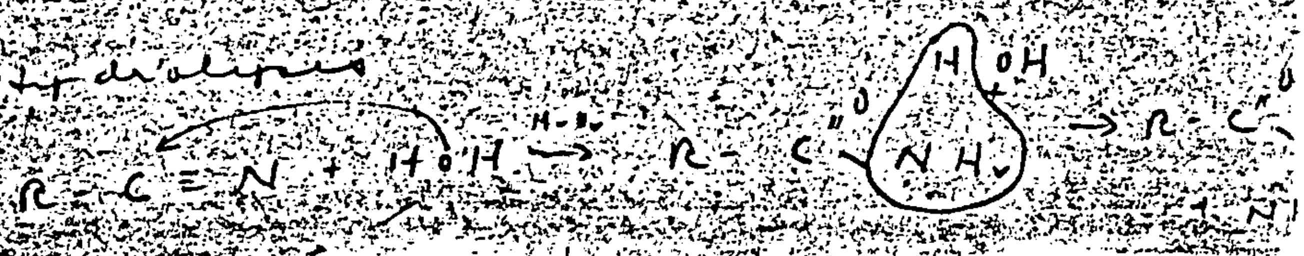


$$CH_3-O-\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}-O-CH_3 + KCN \rightarrow CH_3-O-\overset{O}{\overset{\|}{\underset{|}{S}}}-OK$$

at higher temp both alkyl groups react

Reactions

1. Hydrolysis



$$R-C\equiv N + HOH \xrightarrow{H^+} R-\overset{O}{\overset{\|}{C}}-NH_2 \rightarrow R-\overset{O}{\overset{\|}{C}}-$$

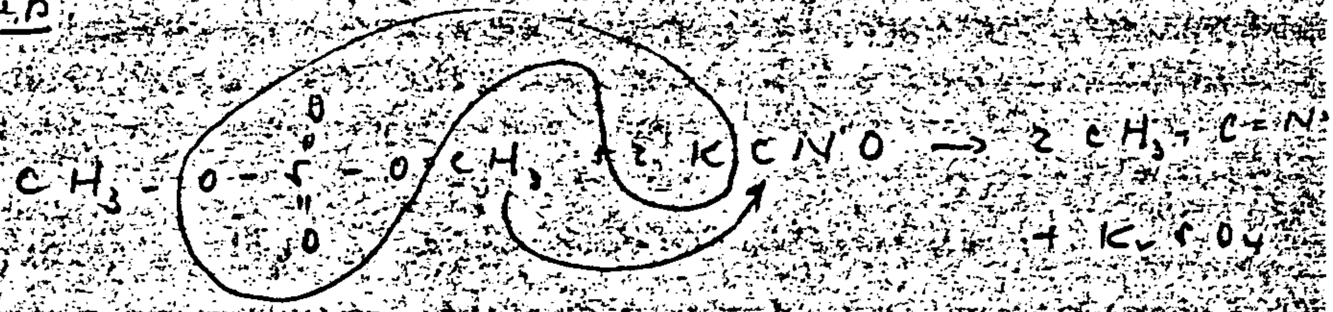
Special Cpds

1. Isocyanides

$R-N=C + O \rightarrow R-N=C=O$

isocyanide — isocyanate

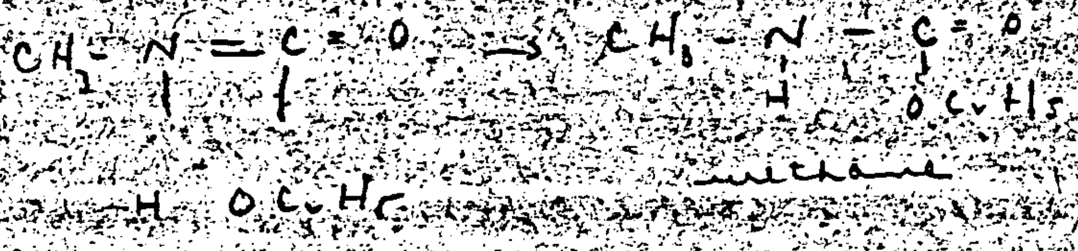
Prep



$CH_3-O-\overset{O}{\underset{O}{S}}-O-CH_3 + 2\,KCNO \rightarrow 2\,CH_3-C=N + K_2SO_4$

Reactions

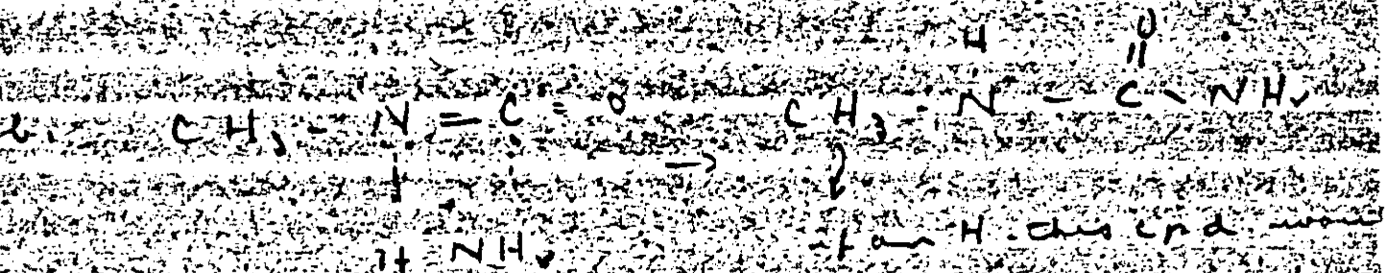
a.



$\underset{H}{CH_3-N}=\underset{OC_2H_5}{C}=O \rightarrow CH_3-\underset{H}{N}-\underset{OC_2H_5}{C}=O$

urethane

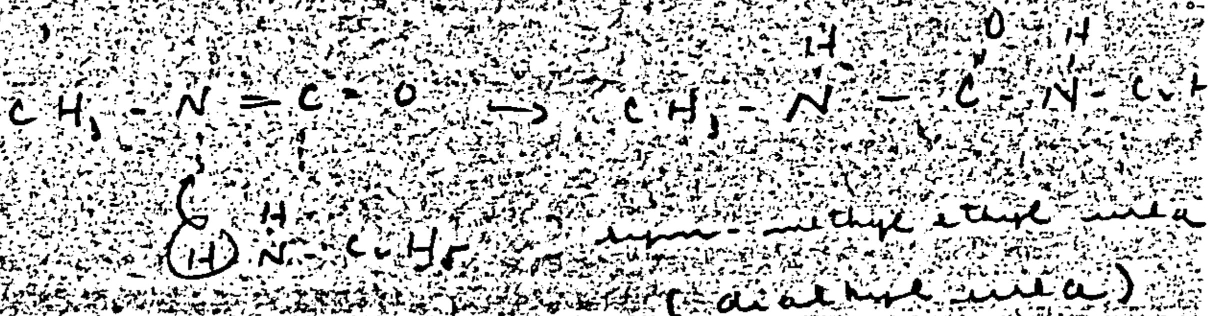
b.



$\underset{H}{CH_3-N}=\underset{NH_2}{C}=O \rightarrow CH_3-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-NH_2$

if an H this cpd would be urea ∴ call it alkyl urea.

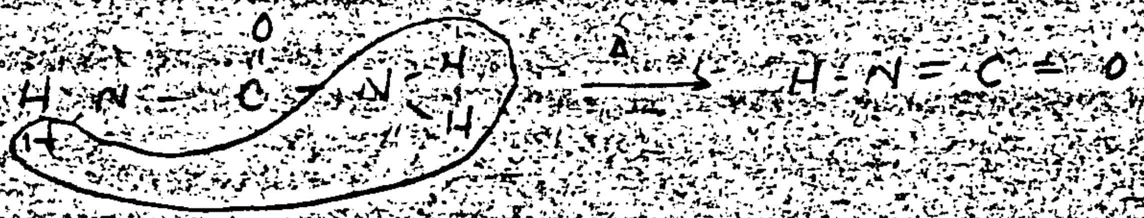
c.



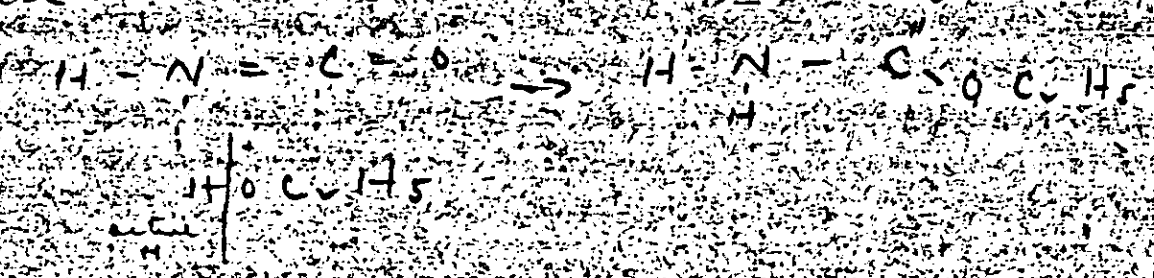
$\underset{H}{CH_3-N}=\underset{\overset{H}{N}-C_2H_5}{C}=O \rightarrow CH_3-\overset{H}{N}-\overset{O}{C}-\overset{H}{N}-C_2H_5$

sym-methyl ethyl urea (dialkyl urea)

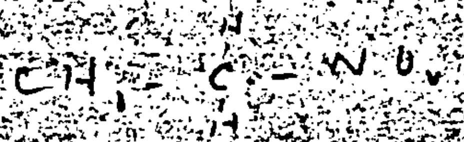
d. prep. urethane (another way)

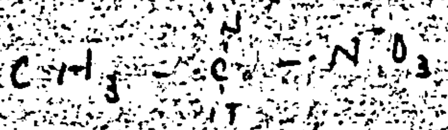

$$H_2N-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{\Delta} H-N=C=O$$

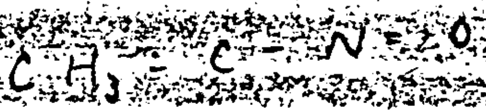
and

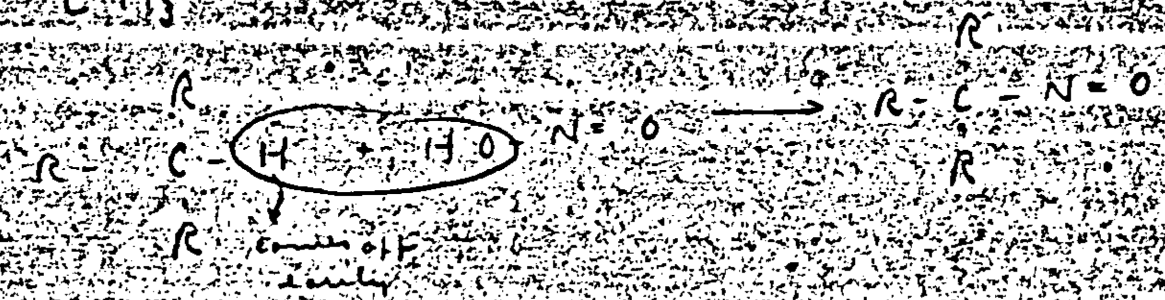

$$H-N=C=O + HOC_2H_5 \rightarrow H-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-OC_2H_5$$

2. nitro cpds

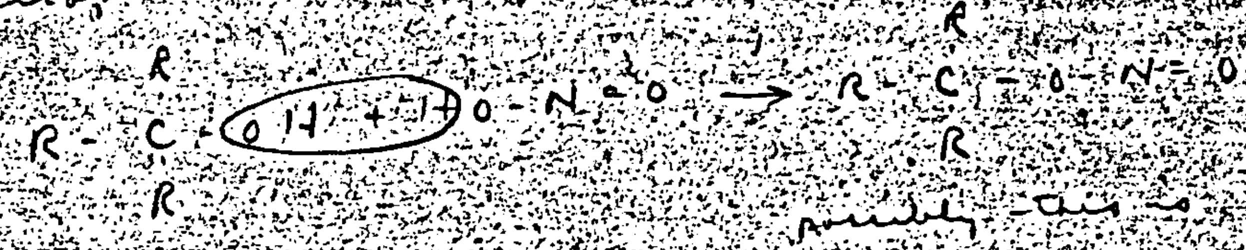

$$CH_3-\underset{H}{\overset{H}{C}}-NO_2$$
nitro group


$$CH_3-\underset{H}{\overset{H}{C}}-NO_3$$
nitrate group


$$CH_3-C-N=O$$
nitroso group


$$R-\underset{R}{\overset{R}{C}}-H + HO-N=O \rightarrow R-\underset{R}{\overset{R}{C}}-N=O$$
comes off easily

also,

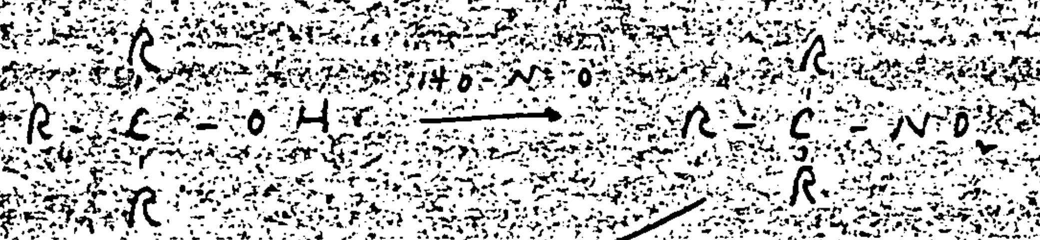

$$R-\underset{R}{\overset{R}{C}}-OH + HO-N=O \rightarrow R-\underset{R}{\overset{R}{C}}-O-N=O$$

possibly this is

or $-N\overset{O}{\underset{O}{=}}$

Reactions

a, Test 1°, 2°, or 3° alcohol



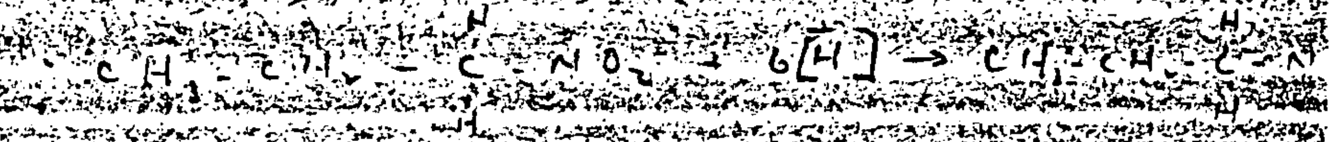
$$R-\underset{R}{\overset{R}{C}}-OH \xrightarrow{HO-N=O} R-\underset{R}{\overset{R}{C}}-NO_2$$

alkali solution

+ KNO_2, then add H_2SO_4 drop by drop

$\longrightarrow$
- blood red → primary alcohol
- blue to green → secondary alcohol
- no color → tertiary alcohol

b, Reduction



$$CH_3-CH_2-\underset{H}{\overset{H}{C}}-NO_2 + 6[H] \rightarrow CH_3-CH_2-\underset{H}{\overset{H}{C}}-N$$

n propyl amine
([illegible])

$R-\overset{O}{C}-NH_2$
amide group

$R-NH_2$
amine group

Ethers

General Formula $\begin{matrix}R\\R'\end{matrix}\!\!>O$

Nomenclature - named from alkyl groups
oxygen atom.

Synthesis

1. $C_2H_5OH + H_2SO_4 + \Delta$
2. Williamson
   alkyl halide + Ag_2O (dry)
3. alcohol + $Al_2O_3 \xrightarrow[-H_2O]{\Delta}$
4. specials
   a) prep ethylene oxide & reactions with
      alcohols + glycols
   b) Ethylene chlorohydrin + H_2SO_4
   c) dioxane

Chem Prop

1. halogenation
2. splitting with HI
3. PCl_5
4. oxonium salts (HCl)

Ald & Ket

Gen Formula - carbonyl group

Nomenclature { ald { [illegible] formald
[illegible]

Prep

1. oxidation [$K_2Cr_2O_7 + H_2SO_4$] ketone ditto

2. Cu (dehydrogenation) ketone ditto (2°)

ketone ditto

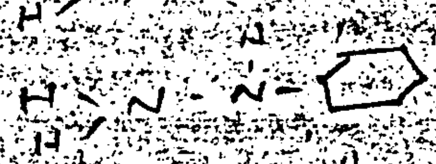
3. [illegible] oxide

4. $H-C\equiv C-H \xrightarrow[H-O-H]{H_2SO_4} CH_3-\overset{O}{\overset{\|}{C}}-H$

Reaction

1. No Boiling
2. M.P. in CCl_4
3. oxidation
4. hydrolysis NaHg
5. reduction

addition Reaction

1. HCN
2. $NaHSO_3$
3. HNH_2
4. $H_2N\cdot OH$
5. 
6. $NH_2-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-NH_2$
7. $HO-N=O$
8. C_2H_5-OH → acetal
9. PCl_5
10. polymerise [illegible] NaOH

65-4307-11-B-[illegible] [illegible]

65-4307

ZF 13

[illegible] #1

A. BROCHMAN & ASSOCIATES

No. 1 of

Date: 10-22-47

By: H. G.

JOB:

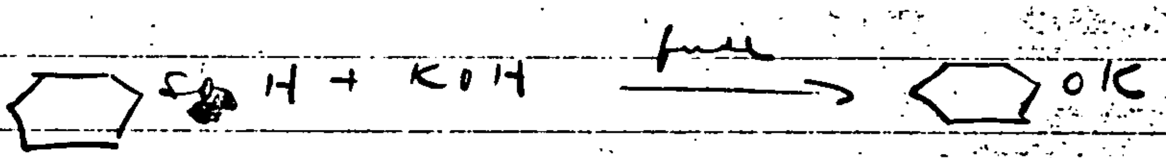
SUBJECT: Vanillin

I Oxidation of to $\overset{\overset{O}{\|}}{C}\diagdown H$

Richter says that $KMnO_4$ will → $\overset{\overset{O}{\|}}{C}\diagdown H$ under carefully controlled conditions, but → no references.

vol II
p.

Richter p. 174 vol II



Thorpe I 664

B.C.A. 1930, 980

{J. Chem. Ind., Russia, 1929, 6, 1439-1440; F.S. Shenderovich & S.S. Livshits)

The optimal conc. of acid is 60%. Rise of temp favors the formation of tar; while below 35° the reaction is slow & more benzoic acid is formed. An excess of hypochlorite may cause the formation of tar during distillation with steam. Prolongation of the reaction tends to increase the relative quantities of benzoic and a tar.

A. BROTHMAN & ASSOCIATES

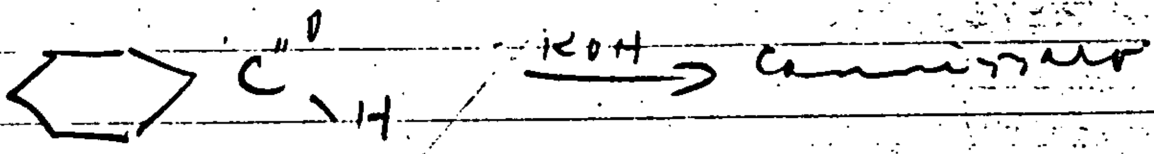
No. 2 of

Date: 12-22-47

By: H.G.

JOB:

SUBJECT: Vanillin



---

methylation of phenol.

Gattermann - Wieland p. 244

1. Diss 0.2 mole phenol 19 g. in 150 cc of 2 N. NaOH in a wide mouthed g-s bottle & add about 1/3 of the 26 g. of $(CH_3)_2SO_4$ to be used. (add in 1 lot.

2. Shake → evol. of heat.

3. add 2nd 1/3 of $(CH_3)_2SO_4$ after 5 min & shake.

4. after "short time" add last of $(CH_3)_2SO_4$

5. Test to see if aq soln on which anisole floats is no longer acid

6. Transfer to distg flask - use 20 cc of NaOH soln as wash.

7. Δ on water bath for 1/2 hr. to complete reaction & to destroy

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Date: 11-22-47

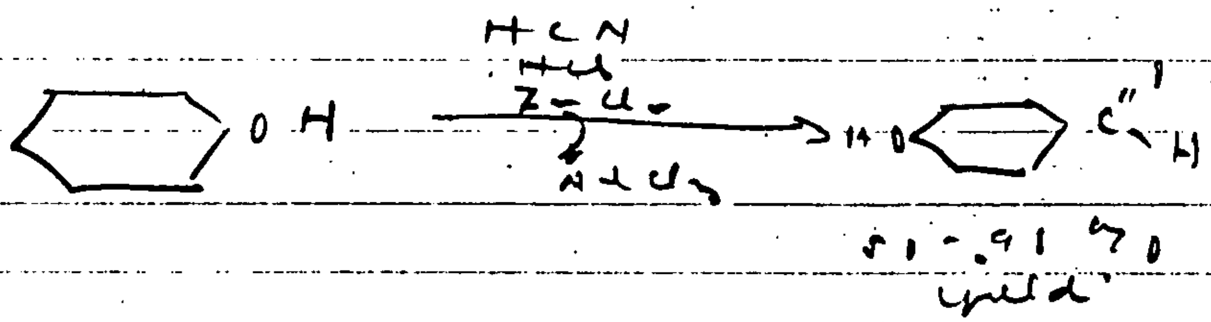
By: H G.

JOB:

SUBJECT: Vanillin

Rice mechanism of Homogeneous org. Reactions

p. 193.



51-91%
yield

Gattermann Ber 31 1765 (1898)
32 278, 284 (1899)
Ann. 357 313 (1907)

Morgan & Vining J. Chem Soc 119, 177 (1921)

Karrer Helv. Chim Acta 2, 89 (1919)

Adams & Levine J.A.C.S. 45, 2373 (1923)
Adams & Montgomery " 46, 1518 (1924)

Richter Vol. II p. 341

1. all phenol aldehydes show the same reactions of the aldehyde group as the benzaldehydes.
2. oxidizing agents convert them with difficulty into phenol-carboxylic acids;

Date: 10-22-47
By: H.G.

JOB:
SUBJECT: Vanillin

this is most easily accomplished by fusion with caustic alkalies

3. or oxidation with dilute alk. H_2O_2 the o- & p- phenol aldehydes split off the aldehyde groups & easily pass into pyro-catechin & hydroquinone (C. 1911 I. 634)

4. They dissolve in alkalies, forming salts, e.g.

; the alkyl iodides convert the latter to alkyl ethers.

Gattermann Synthesis of Hydroxy aldehyd

J.A.C.S. 45, 2373 (1923)
R. Adams & I. Levine

1. A & L. state that big disadvantage of method is use of anhyd. HCN.
2. Karrer gets around this by using BrCN but yields are poor.
3. A & L. propose $Zn(CN)_2$ & use this method. — $Zn(CN)_2$

a. Dissolve tech NaCN (calc. as 100% pure) in 25%, more than an equal wt of H_2O

A. BROTHMAN & ASSOCIATES

JOB:

SUBJECT: Vanillin

Date: 10-22-47

By: H. G.

b. add $MgCl_2$ soln. until no more ppt. of $Mg(OH)_2$ & $MgCO_3$ forms. (This requires an amt. of $MgCl_2$ sufficient to ppt. a quantity of Na_2CO_3 equiv. to 7-8% of the NaCN used).

c. Filter off the ppt. immediately.

d. add filtrate at once to 1 equiv. mole of $ZnCl_2$ diss. in as little as possible of 50% EtOH.

e. Filter off the $Zn(CN)_2$

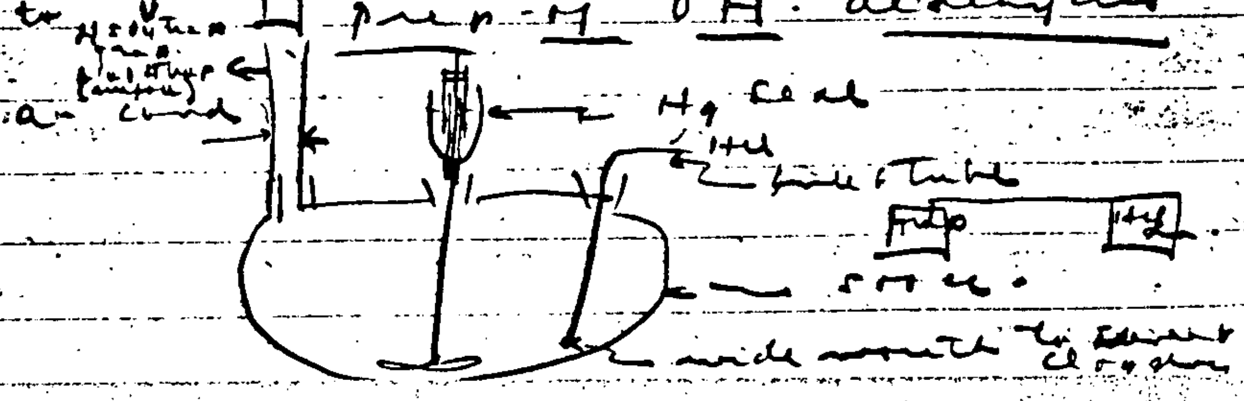
(Note must filter $Mg(OH)_2$ & $MgCO_3$ immed. to prevent formation of dark colored $Zn(CN)_2$)

f. Wash $Zn(CN)_2$ with alc & ether — then dry in air at 50°C.

g. only imp. thing is to assure an excess of $ZnCl_2$ over NaCN — otherwise get sticky mass.

h. Product 91% $Zn(CN)_2$ + 10% — mostly NaCl. Use as is —

prep. of OH. aldehydes



A. BROTHMAN & ASSOCIATES

No. [illegible] of

Date: 11-22-47

By: H G.

JOB:

SUBJECT: Vanillin

b. add 20 g of OHφd. diss in 150-200cc of dry Et_2O.

c. add sufficient dry $Zn(CN)_2$ equiv to 1.5 mol for every mol of phenol.

d. start agitator & pass in HCl (dry) rapidly. The $Zn(CN)_2$ disappears with the formation of a milky sol. (NaCl [illegible])

e. more HCl dissolves the imide chloride seps. as a thick oil.

f. Takes 15-20 mins to sat. with HCl.

g. then pass in HCl more slowly & continue to stir for ½ hr. more to be certain that all phenol has reacted.

h. Decant Et_2O from solid & mix the oil & dec. as below

Yields
resorcyl aldehyde 95%
β-Naphthol aldehyde 85%

i. add 100 cc of HOH to imide-HCl & raise to b.p.

j. filter mixt immed & allow filtrate to cool → 50% yield

k. filter "j" & allow filtrate to stand 10-15 hrs → 25% yield

A. BROTHMAN & ASSOCIATES

Date: 1-22-47

By: H.G.

JOB:

SUBJECT: Vanillin

J.A.C.S. 46, 1518 (1924)

R. Adams & C. Montgomery

modifications in usual procedure

1. using 96–98% KCN no $MgCl_2$ was needed & the $Zn(CN)_2$ was 95–98% pure.
2. Dis. phenol in 5 vols of dry C_6H_6 (5.9) (better stirring)
3. use $Zn(CN)_2$ equiv to 2 moles for every mole of phenol or phenol ether.
4. cool & start unit
5. pass in HCl rapidly for 1/2 hr.
6. cool (& keep so), remove cond. & add 1.5 moles $AlCl_3$.
7. Continue stirring & pass in HCl slowly at 40–45° for 3–4 hrs.
8. add " to an excess of 10% HCl which causes a heavy part of insoluble HCl to sep.
9. Reflux for 1/2 hr → oily product the aldehyde
10. Then either
    a. extract directly
    b. filter from HCl – C_6H_6 mixt.
    c. steam distill & extract from distillate

A. BROTHMAN & ASSOCIATES

No.:

Date: 10-22-47

By: H.G.

JOB:

SUBJECT: Vanillin

11. NaCN → poor yields (also KCN)

Examples

1. anisole

30 g. anisole
52 g. $Zn(CN)_2$
45 g. $AlCl_3$
65 g. C_6H_6
} → 35.5 g. anisaldehyde (Quant.).
b.p. 246–248 °C

a. steam distill after decomp. with HCl
b. Remove C_6H_6 & collect anisaldehyde & anisole fractions.
c. shake with $NaHSO_3$ → addn product.
d. Dec. addn. prod. with $NaHCO_3$ & distil

2. Thymol

21 g thymol
37 g $Zn(CN)_2$
30 g $AlCl_3$
61 g C_6H_6
} 23.5 g aldehyde (quantitative yield).

3.  → ald.
91%, 7 hrs.
b.p. 250–252 °C.

p cresol methyl ether

30 g. 
52 g. $Zn(CN)_2$
45 g. $AlCl_3$
75 g. C_6H_6
}

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No. 1 of

Date: 12-[illegible]-47

By: HG.

JOB:

SUBJECT: Vanillin

anisole

Org Syntheses 9, 12 (1929)
Hiers & Hager 72-75% yield

PCl_5 → p-chloro-cpd.
Cl_2 should give o-Cl deriv of anisaldehyde

Antu

α-Naphthyl Thiourea
specific for Rats
non-Toxic To Humans.

A. BROTHMAN & ASSOCIATES

No. 4 of

Date: 12-22-47

By: H. G.

JOB:

SUBJECT: Vanillin

anisaldehyde   Ullmann. Vol. 8 p. 815

1. carry out this by oxidation of anethol

2. 3 Kg. anisol (contg 80-90% anethol)

3. add 3.6 Kg bichromate mixture

{ 1 Kg $Na_2Cr_2O_7$
  4 Kg. 25% AcOH
  1 Kg conc. H_2SO_4

at 55-60°C. & dis.

4. Heat to 70°C

5. Cool.

6. Filter chrome [illegible]

7. Extract with C_6H_6

8. Purify with $NaHSO_3$

9. Distill under vacuum.

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JOB:

SUBJECT: Vanillin

Date: 10-31-47

By: H. G.

3. Bromo - 4 - Hydroxy - benzaldehyde

ref Beil. 8 (82)

1. Pass in 1 mol wt of Br in cylinder containing well-cooled cooling into a cooled soln of 1 mol wt of p-OH benzaldehyde dissolved in warm $CHCl_3$

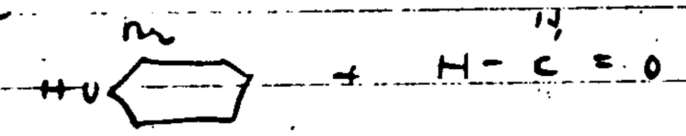
2. Let stand for ½ day.

3. Evap the $CHCl_3$ on a boiling water bath.

4. Crystallize the residue, whereupon the 3, 5 deriv. remains undissolved

orig ref Ber. 28, 2409 (Paal)

alt



$HO\text{-}C_6H_4Br + H-\overset{H}{C}=O$

(Sieger Patent D.R.P. 105,797)
C. 1900 I, 803

Prop

leaflets - from HOH

m.p. 124°C

easily sol. Et_2O, $EtOH$, $EtOAc$, $AcOH$, Me_2CO.

less readily sol. CS_2, $CHCl_3$, C_6H_6

diff sol cold HOH & ~~ligroin~~

more in cold.

A. BROTHMAN & ASSOCIATES

JOB: ( )

SUBJECT: Vanillin

Date: 10-31-4

By: H.G.

3-Cl-4-OH Benzaldehyde

ref Beil. 8, 81

1. pass Cl_2 (theo. calc. amount) into an ice cooled $CHCl_3$ soln of HO

ref orig article

Ber. 37, 4030 (Biltz)

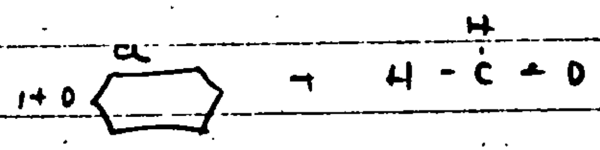
phys prop

1. needles from H_2O

2. m.p. 139°C b.p.$_{14}$ 149-150°C

3. easily sol. EtOH, Et_2O
diff sol. $CHCl_3$
v. sl. sol. cold HOH

also Geigy patent (D.R.P. 105798 C. 1900 I, 503)



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No. 73 of

Date: 12-31-47

By: H. G.

JOB:

SUBJECT: Vanillin

ref Beil. 11, 325

1. pass HSO₃ φ CH₃ into a mixt of MnO₂ & 25% oleum (with an excess of the acid)

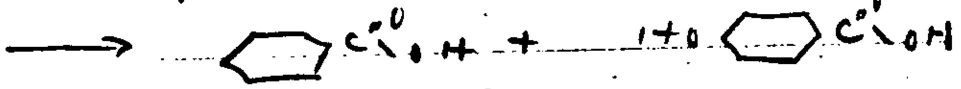
orig article

D.R.P. 154,528

C. 1904 II, 1269

prop

1. Heating with KOH & H₂O at 220-240°C



Ber 39, 2511.

2. Na salt → needles.

ref C. 1904 II, 1269 Kl. 12o. vom 27/4 (1902) [14/10 (1904)

1. 1st dis MnO₂ in oleum

2. Then pass in HSO₃ φ CH₃.

JOB:

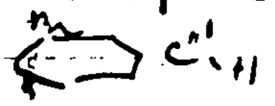
SUBJECT: Vanillin

Date: 10-31-47

By: H.G.

orig. art. Ber 23, 2409 (1890) — C. Paal

1. Diss. p-OH benzaldehyde in 15 times its wt of warm $CHCl_3$.
2. Cool the soln. (some ald. xtallizes)
3. Pass in the theor amt of Br (diss. in $CHCl_3$). add in small portions under agitation & superficial cooling
4. During the bromination a yellow oil seps. out which under the continued evolution of HBr passes into the form of a xtalline substance — the



. P. believes that the oil represents an addition product which then changes into the substitution product. i.e., let reaction mix. stand for ½ day to get a good yield.
5. Filter off the $CHCl_3$ soln.
6. The filtrate contains a considerable quant. of product & this is recovered via evap. of the $CHCl_3$.
7. In order to completely sep. the $CHCl_3$ a ~~transfer~~ product to a porous plate filter & wash with a small amt of HOH

A. BROTHMAN & ASSOCIATES

JOB:

SUBJECT: Vanillin

Date: 10-31-47

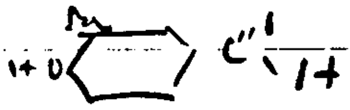
By: H. G.

till all HBr is used.

c- Xtallize several times from boiling HOH.

8 · The yield is quant.

Ber 23, 2411 C. Paal

"On the assumption that the Br atom would easily be substituted than the aldehyde by [illegible] OCH_3, P. heated the  with $NaOCH_3$ in a sealed tube. The reaction takes place only at elevated temps & the minimal yield of product is a badly decomposed mass. Only traces of Vanillin could be found.

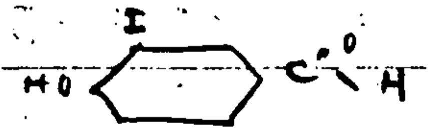
A. BROTHMAN & ASSOCIATES

JOB:

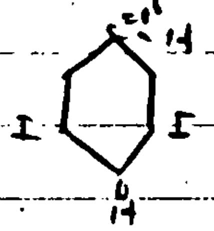
SUBJECT: Vanillin

Date: 11-31-47

By: H. G.



Ref. Beil. 8, 83 lit. No. 746
orig. Ber. 28, 2415 (1895) C. Paal.

1. Herzfeld {ann. di chim. 146, 394}
prep.


& that it was the
mono-I deriv. H. used
1 ~~mol~~ (part) p-OH ϕ C^{O}_{H}
3 ~~mols~~ (parts) I_2 (= 1 mol)
41 parts alc.
61 parts HOH

But if equimolar parts of p-OH ald & I are used then only 1/2 of ther. quant is obtained

2. From #1 above is (~~the~~ ~~[illegible]~~)
is obtained a ~~[illegible]~~
quantity of mono-I-deriv.
m.p. 183°C
dis in alc & Δ HOH
contains: will dis unchanged p-OH ald in Δ HOH.
present in considerable quant.

A. BROTHMAN & ASSOCIATES

JOB:

SUBJECT:

Date: 11·31·47

By: H. G.

Paul obtains Di I deriv by mixing

6 parts p-OH cmd.

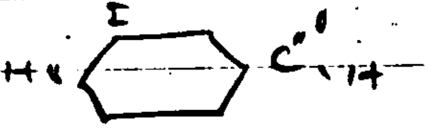
12.5 parts I_2

1.1 part HI

70 parts alc

100 parts H_2O

Δ ~~[illegible]~~ under reflux

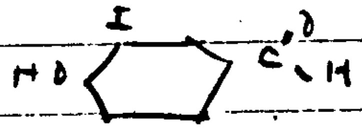


obtained was not prepared by P. in a pure state — He had trouble.

Theor % I 51.21

Found 49.73

no mention is made of forming Vanillin from



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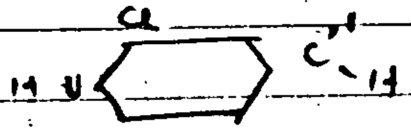


Ber 37, 4052 (1904) H Bilty

1. ~~[illegible]~~ 3 gms p-Cl-OH ϕ C(O)H in 300 gms CH_3 warm & then cool. Filter off whatever ppts appear & cool again (Cis?)

2. Then pass in soln 1 the Cl_2 obtained from 2.7 gm $K_2Cr_2O_7$ & conc. HCl

A. BROTHMAN & ASSOCIATES

JOB:

SUBJECT: Vanillin

Date: 10-31-47

By: H.G.

(This is [illegible] less than the —
excess Cl_2 → di Cl deriv.).
Use vacuum to exhaust Cl_2 from
evolution flask.

3. Let sit for a short time & distill
$CHCl_3$ from a water bath.

4. Xtallize residue from a small amt
of alc → m.p. 154-156°C.

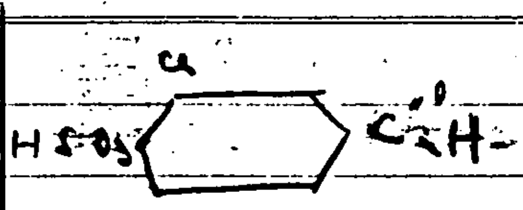
5. Distill under vac = b.p. 149-151°C
(@ 14 mm)

6. Xtallize from HOH → 139°C m.p.
(on long standing drying)
fine white needles.

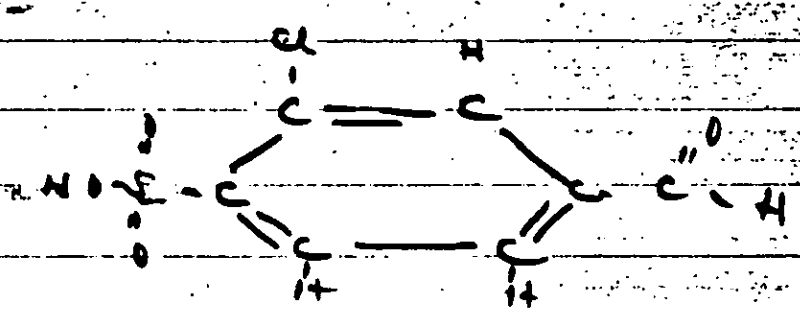
OTHMAN & ASSOCIATES

Date:
By:

SUBJECT: Vanillin



Cmpd No. 1572



$C_7H_5O_4SCl$

Does Not Exist

[illegible]

A. BROTHMAN & ASSOCIATES

JOB:

SUBJECT: Vanillin

Date: 10-31-47

By: H.G.

Ber 39, 2511 (1906) c Graebe & H. Kraft

1. 10 g. ~~NaSO3~~  CHO (9292)

2. Δ with 50 g. KOH + 10 g. HOH @ 220°-240°

3. yield 5.3 g → 2.1 g.  COOH — m.p. 177-180°

3.2 g. HO ⌀ COOH. m.p. 208°C

40% 54%

A. BROTHMAN & ASSOCIATES

Date: 10-31-47

By:

JOB:

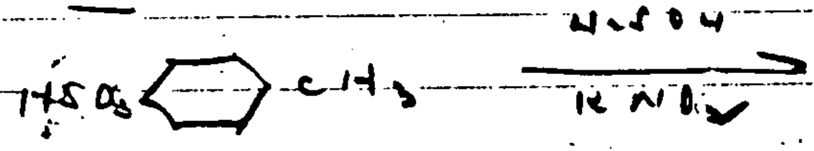
SUBJECT: Vanillin

Vanillin Brit. Pat No. 773 9,248.

Cresol Brit Pat No. 526527 6,399 mm.

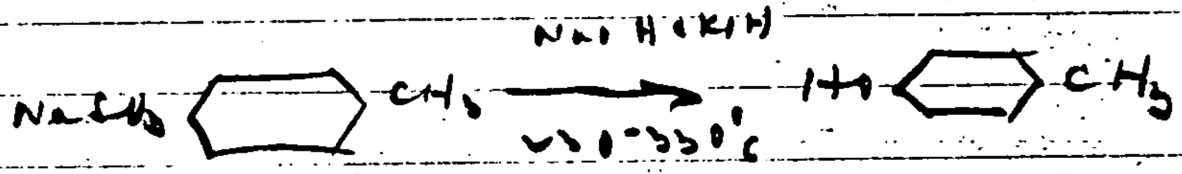
p-Cresol Brit 6,399.

Meth



Brit 6,399 Example 1

Ing. Chem. 2 (1923)



6/6/50

①

4 g. Lanolin

Td 80 g SA

1 gm T.E.A.

~~180°F~~ 20 gms glyc

~~HEE~~

300 g. 140 H

TTEC

C_4H_9 ~~C_2H_5~~ O – CH_2 CH_2 OH

cellosolve

menthol

me salicylate

mennens

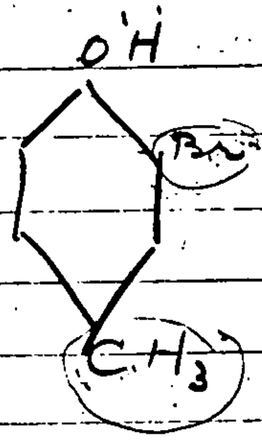
No. of

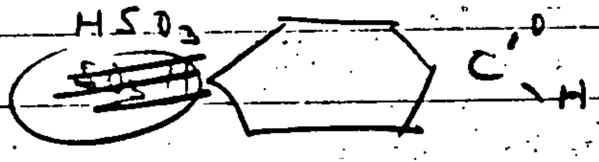
Date:

By:

JOB:

SUBJECT:





#2

JOB:

SUBJECT:

✓ 1. Peacock ✓

✓ 2. Glue Catalyst

✓ ~~3. Patchat~~

✓ 4. Vanish. Cream ie

✓ 5. Extraction - Send for Sample

6. methyl methacrylate Synthesis

7. Patent Work on methyl methacrylate

~~1. Peacock~~ ✓

~~A. Emulsion~~ ~~make out with Tergitol~~

B. Get
- Tweens
- Twitchell Base
- Santomerse
- Nacconal - Natl Aniline
- Duponol - alcohol sulfate
- alkyd resins

Santopour
Paraflow

~~C. Idea of Konga Confree (by Crawing)~~

D. Take unsized paper & coat with sizing!

E. mechanical means of applying paste & powder

A. BRO[illegible]HMAN & ASSOCIATES

No.____of____

Date:____

By:____

JOB:____

SUBJECT:____

2. Glue Catalyst
   ~~A. [illegible] content~~ (nill)
   ~~B. water base Protein~~ (nill)
   ~~ask [illegible] mixing~~
   ~~Deter mg.~~

3. Paschal
   ~~a. Finish Research~~
   ~~b. Write Report~~
   ~~c. Lab work ???~~

4. Vanishing Cream
   a. Get { cetyl alc
   carbowax
   propylene glycol
   carbitol
   menthol
   b. Prep. Sample for Consist
   c. Prep Sample for "Tang"

~200 g.

~300 g.

1119 Acids

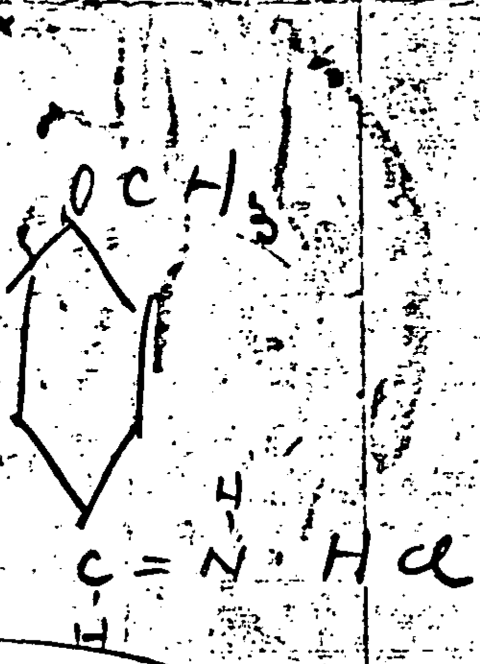
$\frac{117}{136} \times 139 =$

$\frac{133}{107} \cdot 60 = 1.5$

108
+14

1.35 1.0 9

$\frac{36.5}{10} \times$



$\frac{36.5}{108} \times 60 =$

~10 gm HCl

415 cc $\times \frac{38}{10}$

6/6/50

②

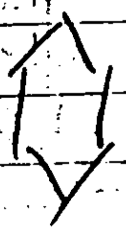
A. BROTHMAN & ASSOCIATES

JOB: [redacted]

SUBJECT:

Date:

By:



~~$\frac{2 \times 149.0}{136.3} \times 50$~~

111

$\frac{136.3}{2 \times 49.0} \times \overset{100}{\cancel{50}} = 139.0$ gm ZnCl₂

$\frac{139.0}{0.98} = 142$ gm ZnCl₂ / 100 g NaCN

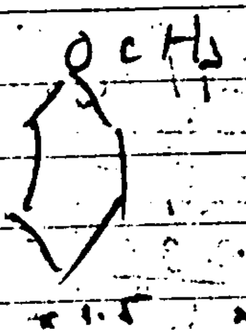
110 g NaCN + 125 cc H₂O

$\frac{40}{108} = .37$ mole

$\overset{5}{\cancel{0}}$

40 g

120 cc C₆H₆



1.5

0.37 × 1.5 × 117.00 = 48 g.

Zn(CN)₂ / they assume

#3

SUBJECT: [illegible]

Ref. Thorpe Vol III p. 09

1. manuf. by reduction of CCl_4 with nascent Hydrogen.
2. method — stir a mixture of CCl_4 and finely divided Fe in water; the reaction is initiated by the addition of a small amt. of HCl.
U.S. Patents { 783,325 / 1,107,025.

Ref. Ullmann

1. can control reaction (above) by energetic stirring & [illegible] any CH_2Cl_2 from forming. This process is used in the U.S.
2. also E.P. 586,006

a. 1700 g. $FeSO_4 \cdot 7H_2O$
5000 cc H_2O

b. add 1750 cc 36°Bé NaOH
& 500 gms. CCl_4

c. warm gradually under stirring till b.p. of $CHCl_3$ is reached.

d. yield 90%

A. BROTHMAN & ASSOCIATES

JOB:

SUBJECT:

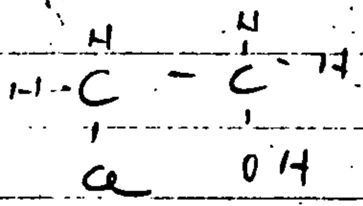
No. of

Date:

By:

abs. complete

31 - 25



$$\begin{matrix} & H & & H & \\ H- & C & - & C & -H \\ & Cl & & OH & \end{matrix}$$

C_2H_5OCl

Beil I . 324

Beil E II 324

	2209^{9}	$2221^{7,8}$
	1719^{7}	2838^{4}
	1944^{5}	2843^{4}
24	$2554^{7,8}$	3089^{4}
	$2842^{8,9}$	4122^{2}
	3091^{1}	
		4306^{8}
	3778^{3}	935^{5}
	$3058^{4,5}$	1476^{9}
23	$3547^{2,3}$	
	$4028^{1,2}$	

#4

A. BROTHMAN & ASSOCIATES

JOB:

SUBJECT:

Date:

By:

Eimer & Amend

✓ 9-191-5	1 pkg (200cc) 6 mm. Berl saddles	$3.25
✓ 14-097	— Rubber gloves, Neoprene, heavyweight Size 9	1.40
✓ 14-836-1	Alkacid test paper, box of 4 rolls	1.00
✓ 3-565	3 Brush, swivel joint	0.75
? 3-636	1 doz. Brush, tube, soft bristle	0.75
✓ 11-162	1- Flowmeter, pyrex	6.80

✓ Percchen # E-139 - 1 gal

acid H_2SO_4 # A-300 1 lb

HCl 6 lb.

✓ 1 lb $NaHCO_3$ c.p.

✓ 1 lb # S-233

1 lb $CaCO_3$ powder # C-62

✓ # 2-190 balance dish

[illegible]

A. BROTHMAN & ASSOCIATES

JOB:

SUBJECT:

Date:

By:

SGA

~~17820~~	~~1~~	~~dz. rubber bulbs for droppers~~	~~0.15~~
~~17825~~	~~3~~	~~1/2 oz~~	~~0.30~~
	~~2~~	~~3 oz "~~	~~0.50~~
~~17805~~	~~2~~	~~Rubber bulb for pressure only~~	~~0.60~~
~~17810~~	~~1~~	~~" for vacuum or pressure~~	~~0.60~~
~~17800~~	~~2~~	~~Extractor rings, size #4~~	~~0.50~~
	~~3~~	~~" " 5~~	~~0.60~~
~~17790~~	~~2~~	~~asbestos rings, 3" O.D.~~	~~0.34~~
	~~2~~	~~" " 4½" O.D.~~	0.54
	~~2~~	~~" " 5½" O.D.~~	0.80
19125	24	test tubes, pyrex 150x18 mm.	1.08 ~~0.86~~
	~~12~~	~~" " 175x22 "~~	~~0.78~~
~~19145~~	~~6~~	~~" 9x1~~	[illegible]
~~9705~~	~~3~~	~~pyrex funnel 60°, 50 mm diam~~	0.81
	3	" " " 75 " "	1.02
	~~3~~	~~" " " 100 " "~~	~~1.25~~
~~9735~~	~~2~~	~~pyrex funnel stems 50 mm diam~~	~~0.44~~
	~~2~~	~~" 100 mm.~~	~~0.22~~

Glass Büchner funnels.

~~1370~~	~~6 1~~	~~Griffin beakers, 600 cc.~~	~~1.56~~
~~9010~~	~~1~~	~~filter flask 250 cc~~	~~0.70~~
~~9010~~	~~1~~	~~500 "~~	[illegible]
~~9010~~	~~1~~	~~1250 "~~	[illegible]

C O

#5

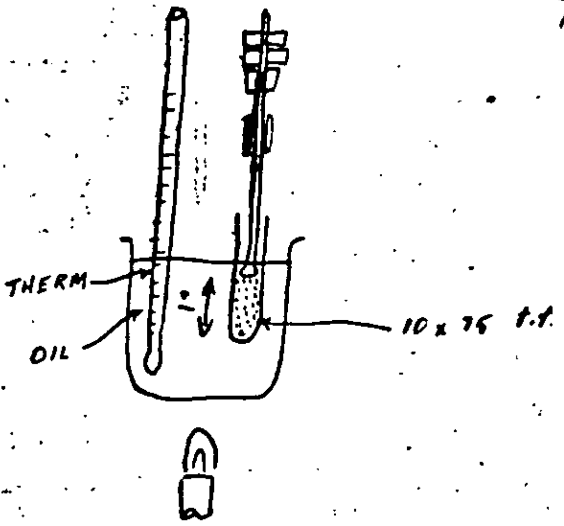
22 Aug 47

A. BROTHMAN & ASSOCIATES
Chemical and Mechanical Engineers
114 EAST 32nd STREET
NEW YORK 16, N. Y.

Flow point of ground Lot 54 molding powder
13 × 100 t.t.
0.145" plunger, 373 g wts.

Time	Temp	Remarks
4:10 PM	125 °C	Beginning of const. temp. period
4:25 PM	125°C	Insert plunger & begin heating.
:28		1/4" fall on putting weights on plunger.
:32	128°C	1/8" fall
	132°C	1/4" fall
:39	138°C	3/8" fall
:46	146°C	1/2" fall
:53	153°C	5/8" fall

Standardization of molding powder test:



Heating: Heat rapidly to 120° C.
Hold 10 min.
Heat @ 1°/min to flow point
Flow point taken as point at which plunger has sunk 5/8".

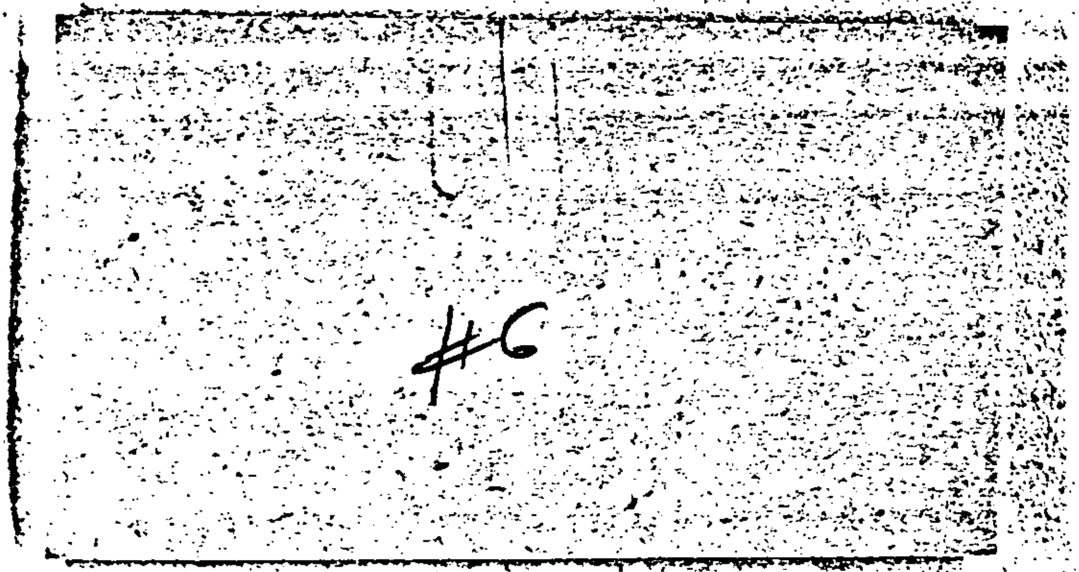
Results:
Ground R & H injection powder: 149°C
Lot No. 54, ground: 186°C
R & H compression powder: No flow point. Originally plunger sank, then rose again.

The apparatus was then modified as follows:

1) A 18 x 100 test tube substituted for 10 x 75
2) This tube filled initially to 1 1/2".
3) Flare on plunger eliminated. Plunger 0.145" diam Plunger + weights = 373 g.
4) Plunger only put in after material is at 120° & tacky enough to prevent sliding in of plunger without compression of particles. Flow point (5/8" plunger sinking) is measured from 30 sec after plunger inserted.

Results: R & H comp. powder: 157° C, 160°C, 166°C (last sample tamped too much originally)

Lot # 54: 148°C Is this due to larger particle size than R & H or to lower FT?

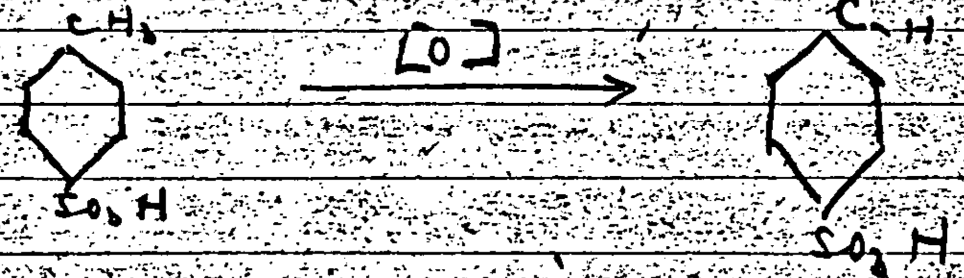


#6

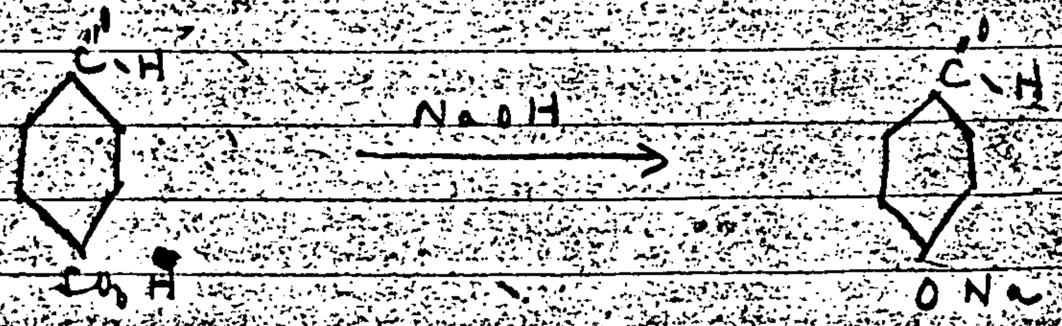
Work to be Done

It was decided to investigate the feasibility of carrying out the following general reactions with a view to producing certain substituted aromatic aldehydes:

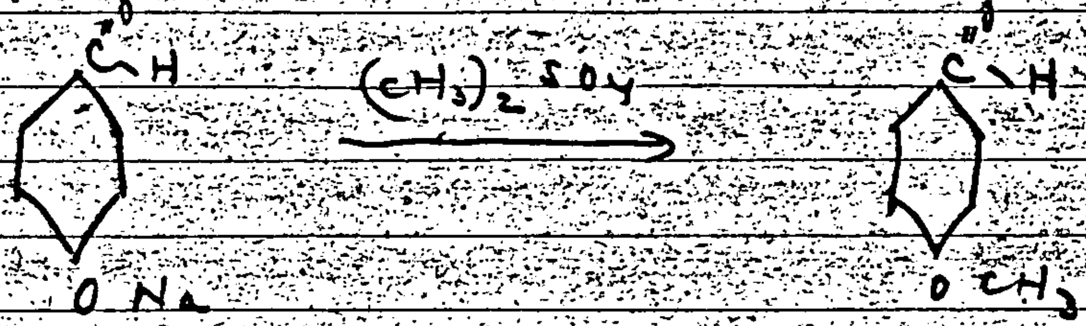
1. The oxidation of a methyl group (present in the para position on a ring to a sulfonic acid radical) to an aldehyde structure, i.e.,



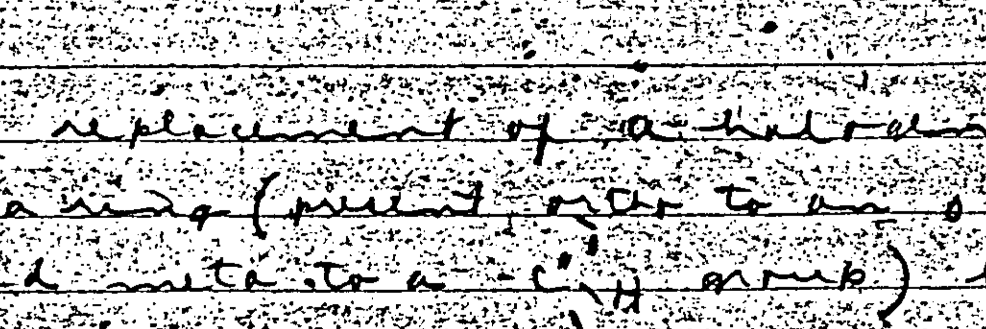
2. The replacement of a sulfonic acid group (present in the para position on a ring to an aldehyde group) by an OH linkage, i.e.,



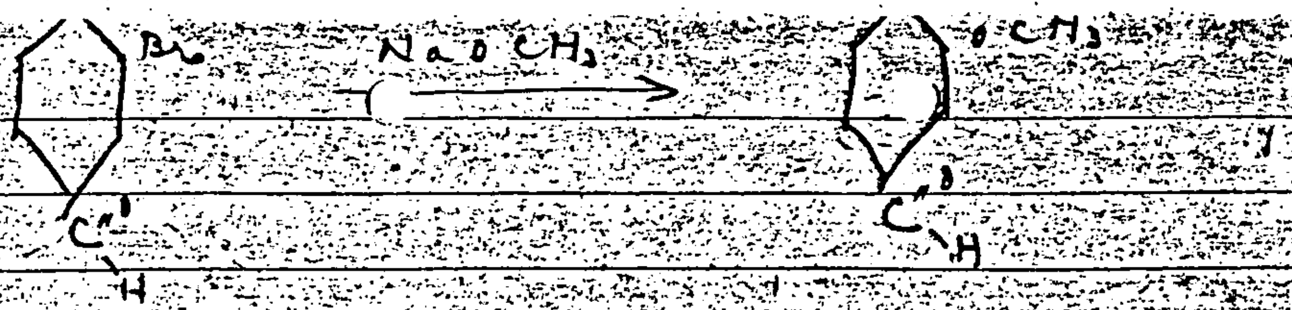
(present in the para position on a ring to an aldehyde group) to an alkyl ether structure, i.e.,



4. The halogenation of an aromatic hydroxy aldehyde (with the OH para to the $\overset{O}{C}H$ group) to yield a monohalogen derivative with the halogen substituent ortho to the OH group, i.e.,

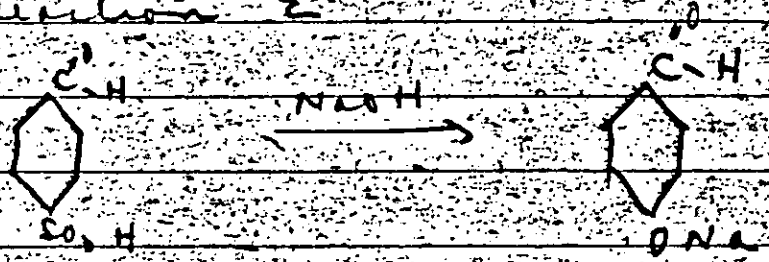


5. The replacement of a halogen group on a ring (present ortho to an OH group and meta to a $\overset{O}{C}H$ group) by an OR (R = alkyl group), i.e.,

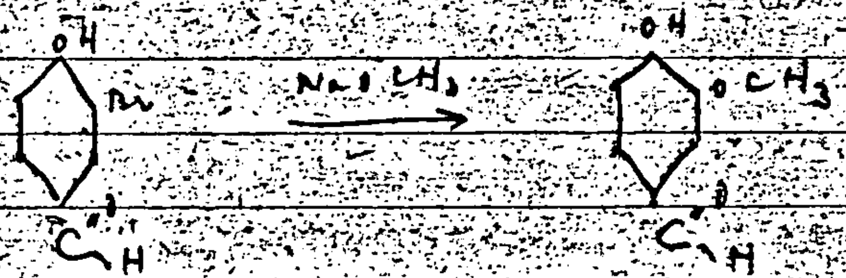


The basis for a successful accomplishment of the above work has been thoroughly gone into, both from the standpoint of a chemical literature search (and by some laboratory work). The results may be summarized thus:

1. Reaction 2



and Reaction 5



cannot be carried out to give any significant yield of the products desired.

2. Reactions 1, 3, and 4 are practical

for the conditions involved

3. an alternative method for the production of anisaldehyde is given.

4. The proposed course of any further work directed toward a successful solution of the problem of a low cost method for the production of substituted aromatic aldehydes is detailed.

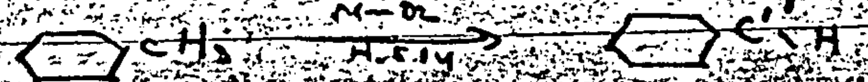
I Investigation of Individual Reactions

A. Oxidation of p-Toluene sulfonic acid to p-Benzaldehyde sulfonic acid —

Two methods are described in the literature for the conversion of the ~~a~~ methyl group on ring to the aldehyde structure by means of the cheap and readily available MnO2 (pyrolusite)

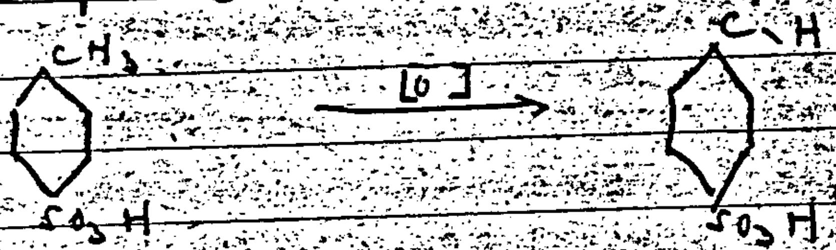
Ref ① J. Chemical Industry of Russia Vol. 6, p. 1439-1440 (1929)
T.S. Shindelrovich and S.S. Livshits
(original article)

British Chemical Abstracts 1930 p. 98

reaction


2. rise of temp. favors the formation of tar, while below 35° C, the reaction is slow and more benzoic acid is formed.

3. an excess of pyrolusite may cause the formation of tar during the distillation with steam (this problem would not be encountered in the case of the reaction)



as the sulfonic aldehyde produced is soluble in water).

4. Prolongation of the reaction tends to increase the relative quantities of benzoic acid and tar.

Ref ② German Patent 154,528
Kl. 12o
applied for April 27, 1902
granted October 14, 1904
(original article)

Beilstein 11, p. 323
Chemische Zentralblatt 1904, II, p. 126

1. First dissolve MnO_2 in 25% oleum — use an excess of the acid.

2. Then pass in the 

Evaluation:

1. The method of [illegible] and [illegible] would seem to be the one most likely to work successfully. It does not seem as though the fact that the oxidation here was carried out on toluene would give any different results were the p-toluenesulfonic acid used.

2. The German patent appears to have the flaw in it that the use of 25% oleum might very likely result in further sulfonation. However, this much is true:

a. MnO_2 dissolves in 95% H_2SO_4 and in oleum with the formation of (a green colored) manganese heptoxide Mn_2O_7 which very readily gives up its oxygen even at low temperatures.

b. So, by the use of the proper time and temperature conditions it may be possible to oxidize the CH_3 group and separate the product before any appreciable sulfonation can

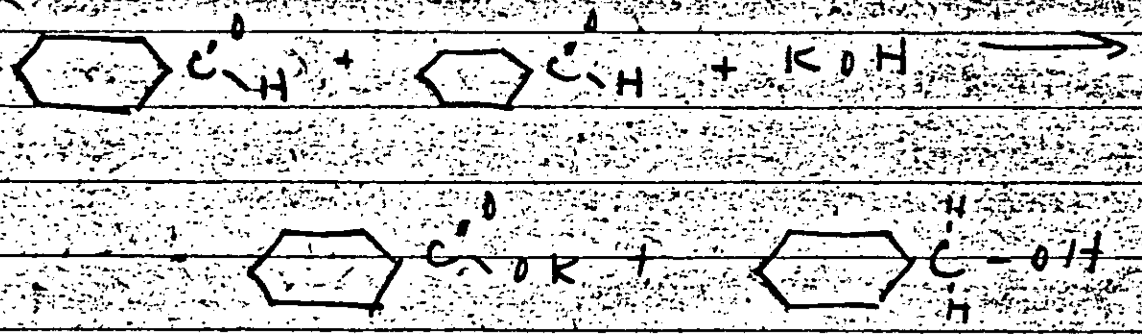
3. no yields are given for either reaction though the (original articles) may state values.

B. The conversion of p-Benzaldehyde sulfonic acid to p-Hydroxy Benzaldehyde.

Literature Background — Ref ① Organic Chemistry by Frank Whitmore

p. 791

1. alkalies cause the Cannizzaro reaction to take place with an aromatic aldehyde



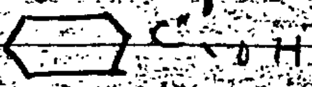
2. If the aldehyde is entirely peroxide free, the reaction does not take place (Kharasch 1935)

Ref ② Berichte 39, p. 2511 (1906)
C. Graebe and H. Kraft

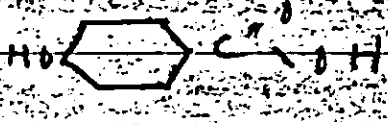
1. Take 10 gms of $NaSO_3$  (92
This is the technical grade. A + K.

2. Heat 50 g. of KOH and 10 gms of HOH at 220-240°C.

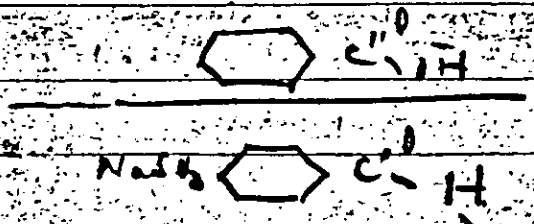
3. yield (total) - 5.9 gms. of product, which

a - 2.1 gms.  46% of theo.

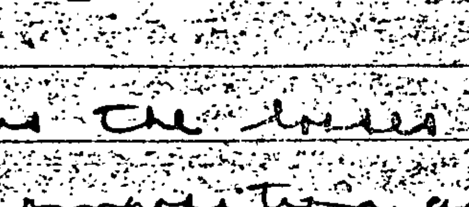
on acidification →

b - 3.3 gms.  51% of theo.

There should have been obtained

a -  x 9.2 = $\frac{122}{194}$ x 9.2

= 5.8 gms.

b -  9.2 = $\frac{138}{194}$ x 9.2

= 6.5 gms.

Thus the losses entailed due to decomposition are considerable.

Evaluation:

1. The work of Graebe and Kraft shows

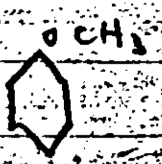
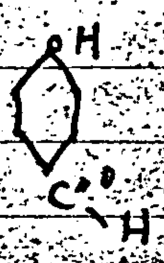
group on (an aromatic) aldehyde is not a feasible one due to the extreme conditions required and under which the $\overset{O}{C}{-}H$ group either

a- is oxidized completely to $\overset{O}{C}{-}OH$

b- or is decomposed entirely

2. The work of Kharasch should be looked up to see whether by elimination of the peroxide from the aldehyde, the tendency of the  to undergo a Cannizzaro reaction can be eliminated.

C The formation of anisaldehyde from from p-Hydroxy benzaldehyde.

Literature Background. The reference given below refers to the preparation of anisole  from phenol but it most likely can be used to prepare anisaldehyde from 

G. Hiers and F. Hager

1. add 235 gms of phenol (2.5 mols) and 100 gms of NaOH (2.5 mols) to 1000 cc. of water
2. Cool to below 10°C
3. Then add 315 gms (2.5 mols) of $(CH_3)_2SO_4$ over a period of 1 hr. The reaction must should be kept bet. 20-25°C all of this time
4. Heat the mixture to 100°C for a ½ hour.
5. Then add 2.5 moles more of phenol over a 75 minute period
6. Then reflux for 15 hrs.
7. Cool the mixture
8. Separate the anisole layer.
9. Extract the water layer with benzene and add it to the anisole
10. Strip off the benzene
11. Distill the anisole under vacuum (b.p. 153-154°C at 749 mm)
12. yield (based on dimethyl sulfate) — 75%

chemistry 24th ed.
( )
by Gattermann and Wieland
p. 244.

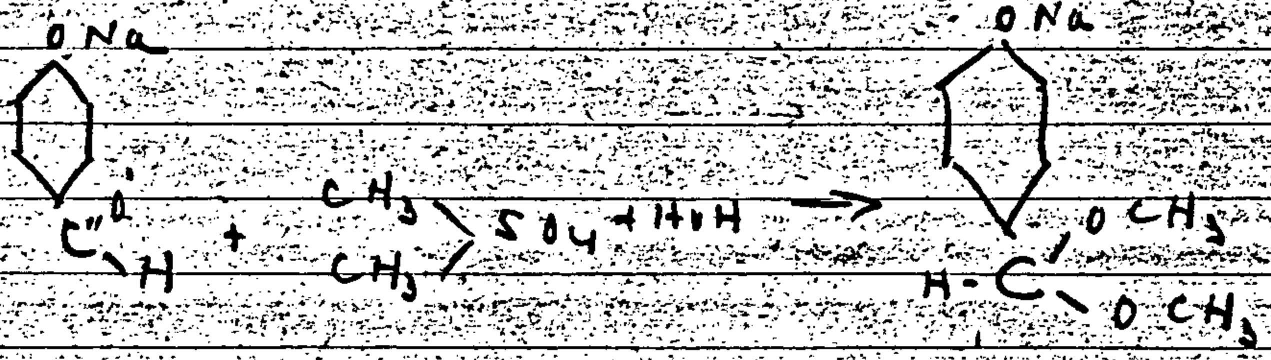
1. dissolve 0.2 mol (19 gms.) of phenol in 100 cc of 2N NaOH
2. add 26 gms of $(CH_3)_2SO_4$ in $\frac{1}{3}$ portions over 5 minute intervals and under agitation
3. Test to see if the aqueous solution on which the anisole floats is no longer acid.
4. add 20 cc of 2N NaOH and heat at 100°C for $\frac{1}{2}$ hour to complete the reaction and destroy any $(CH_3)_2SO_4$
5. cool and remove the aqueous layer
6. Dry the anisole and distill
7. yield (based on phenol) = 90%

Evaluation

1. The method of Hess and Hagle utilizing as it does both CH_3 groups of dimethyl sulfate appears to be the more logical choice
2. The technique would probably not

which the product (anisaldehyde) boils at 247°C as against 154°C for anisole

3. The only drawback to the process may be the possible formation of aromatic acetals



but this reaction does not seem very likely as it is not mentioned in Whitmore's, Victor von Richter's and Meyer-Jacobson's Texts. Still a further search should be made in Beilstein and the more recent literature. Very likely, however, the conditions for the reaction could so be set as to hydrolyze the acetal as fast as it is formed.

D. The preparation of 3-Bromo-4-Hydroxy-Benzaldehyde from p-Hydroxy-benzaldehyde.

Literature Background: Reaction data for the synthesis of both the Br and Cl derivatives of p-Hydroxybenzaldehyde are given.

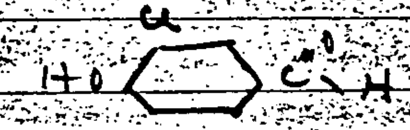
C. Paal

1. Dissolve p-Hydroxy benzaldehyde in 15 times its weight of warm $CHCl_3$.
2. Cool the solution (some aldehyde crystallizes out)
3. Add the theoretical amount of Br_2 (dissolved in $CHCl_3$). The addition should in small portions and under agitation and some cooling
4. During the bromination a yellow oil separates out which, under the continued evolution of HBr, passes into the form of a crystalline substance — the  P believes that the oil represents an addition product which then changes into the substitution product. Therefore, the reaction mixture should be let stand for $\frac{1}{2}$ day in order to get a good yield.
5. Filter off the $CHCl_3$ solution
6. The filtrate contains a considerable quantity of product and this is recovered on the evaporation of the $CHCl_3$.
7. Add the residue from the $CHCl_3$

to the main portion of product and wash under vacuum (   ) with a small amount of cold water till all of the HBr is separated

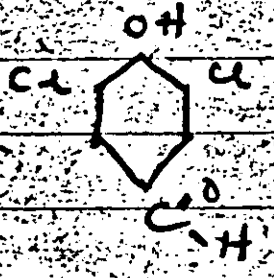
8. Crystallise several times from boiling water

9. The yield is quantitative

Ref ② Preparation of 

Berichte 37, p. 4032 (1904)
H. Biltz

1. Dissolve 3 gms of p-Hydroxybenzaldehyde in 300 gms of warm $CHCl_3$. Filter off whatever crystals appear and cool again

2. Then pass in over a one hour period the Cl_2 obtained from 3.7 gms of $K_2Cr_2O_7$ and conc. HCl (This is somewhat less than the theoretical amount; excess Cl_2 would yield ). Use a slight vacuum to exhaust the Cl_2 from the evolution flask and to pull it into the reaction flask

the $CHCl_3$ from a water bath.

4. Crystallize the residue from a small amount of alcohol to yield a material with an m.p. of 134-136°C

5. Distill the material under vacuum — take the fraction boiling at 149-150° at 14 mm.

6. Again crystallize the product from water. Fine white needles result m.p. 139°

7. no yield is given

Evaluation

1. The preparation of the bromine derivative would seem to be the best choice in spite of the relatively high price of Br_2 (21 cents/lb.) because the replacement of the Br by an OCH_3 should take place far more readily than in the case of the Cl compound.

E. Reaction of 2-bromo-p-cresol with sodium methoxide to yield Vanillin.

iterature — The references given below not
ackground only refer to the direct preparation of vanillin but to the whole

[illegible] of the [illegible]
halogen atom on a ring.

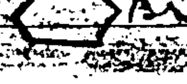
ref ① Berichte 28, p. 2411 (1895)
C. Paal

on the assumption that the Br atom could more easily be substituted than the aldehyde group by $NaOCH_3$, Paal heated  with $NaOCH_3$ in a sealed tube. The reaction takes place only at elevated temperatures and the principal yield of product is a badly decomposed mass. Only traces of vanillin could be found.

ref ② Chemisches Zentralblatt 1898 I, p. 439
Vandevelde
and Liebig's Annalen der Chemie 133, p. 49
Fittig

neither heating with H_2O or KOH (even for 6 hrs) produces the slightest change in 

ref ③ Comptes rendus 53, p. 587
Liebig's Annalen der Chemie 121, p. 359
Riche

Heating  for several days with

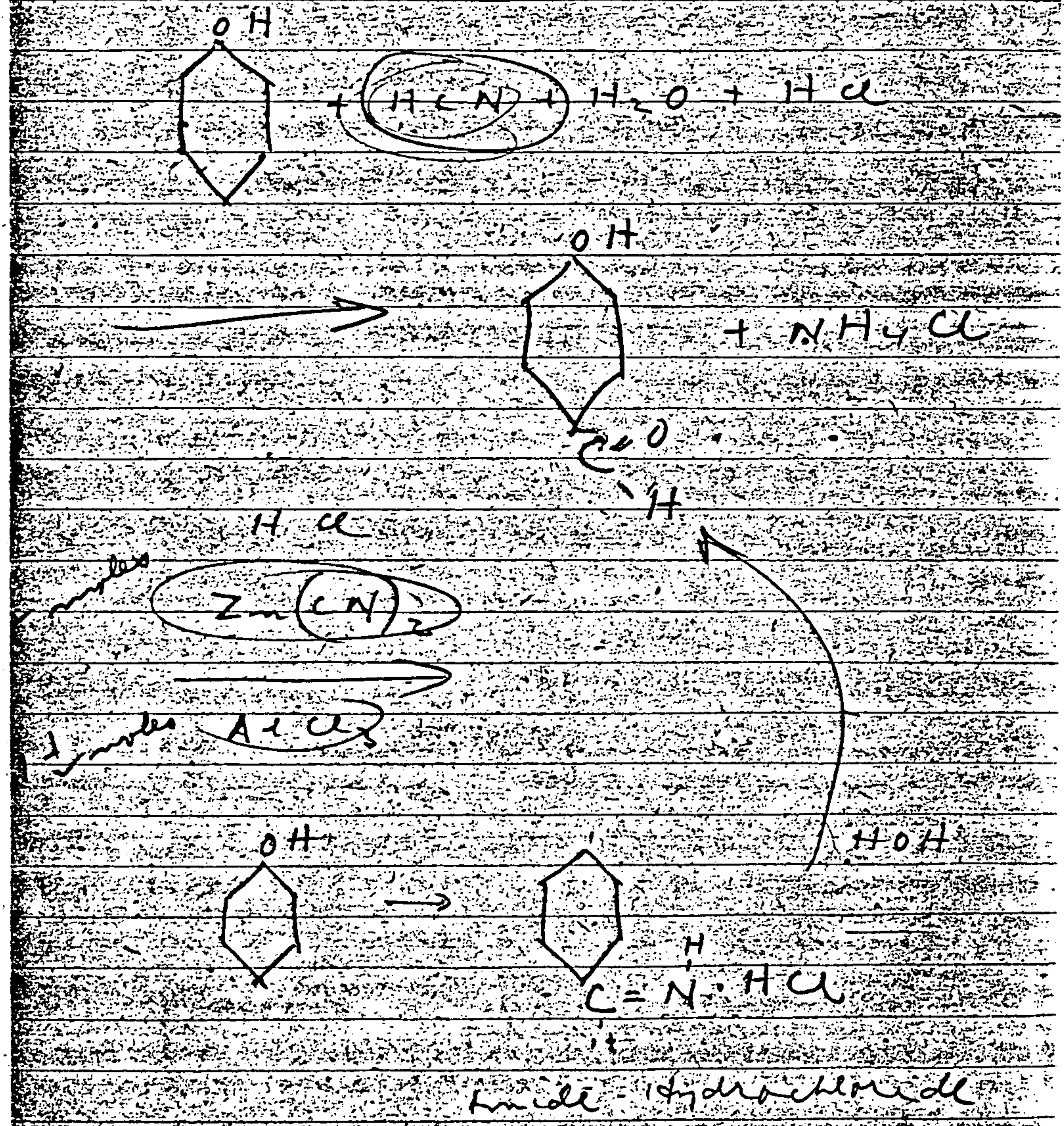
[illegible]

Ref ④ Beilstein 5 (2nd Supplement), p. 120
German Patent 411,052 (Agfa)
when  is heated with NaOH
and MeOH at
25 atmos
170-200°C
for 2-4 hrs
a mixed product of anisole and
phenol is produced

Evaluation

1.

Gattermann Reaction



C O

#7

JULIAN PAUL BRODIE

September 13, 1946

Mr. A. Brothman
A. Brothman and Associates
114 East 32nd Street
New York 16, N. Y.

Dear Mr. Brothman:

This will confirm the understanding in our conversation of August 29, 1946. It is understood and agreed that your organization will undertake to develop for me a men's vanishing cream, subject to the conditions agreed upon between us. It is understood and agreed that your estimate for the work involved will bear a direct total cost of $1200 to $1300, which will be defrayed by me.

It is further understood and agreed that you will incorporate into the finished product ingredients which will have genuine therapeutic effect on the skin.

It is further understood and agreed that the product you submit as final will be tinted a shade subject to my approval, scented with an odor subject to my approval, and will in no wise be irritating or harmful to the skin. A further, and indispensable property of the finished product you develop will be that its application to the skin will leave a slight residue of tan coloring on the skin of the user. Moreover, it is understood and agreed that the final product you submit for my approval must be commercially practical in the sense that it must not be composed of ingredients so costly as to make the final product unmarketable, and that the final product will be commercially possible to compound in quantity, to package in jars, and that it will retain its moisture and its properties for indefinite periods and will not depreciate or lose its efficacy while in packages on dealers' shelves.

In consideration of the fee agreed upon, it is understood that: (1) In lieu of any profit realized by you at this time, you shall receive a stock interest in any company which may be formed to produce and market the product. (2) In the event that the further development of this undertaking should involve the building of plant facilities for the manufacture of the cream, your firm will be given priority consideration in the engineering and designing of the plant. (3) In the event that any special trade secrets or patents shall develop or seem necessary during this work, you shall, for my interest, protect the same to the utmost extent. But it is understood that such secrets and patents shall become my property and assignable by me, at terms within my discretion, to the company which may be formed to exploit this product. (4) It is understood that you will take all steps to the end that the finished product will comply in all respects with such pure food and drug standards as are presently established by law. (5) It is further understood that you are to keep me continuously advised of the progress and development of your work and (6) It is understood and agreed that you will begin immediately on this work, that you undertake to complete it within three months or less and that you will deliver to me a reasonable quantity of your final product for test, consumer study and analysis.

It is understood that you will begin work as soon as this contract is executed by both parties and your signature below constitutes your acknowledgment of the receipt of a retainer payment in the amount of $650. against the total sum named above. The balance will be payable at the time the project is completed in accordance with the specifications of this letter.

I look forward with great interest to the result of your work and assure you of my confidence that you will develop a satisfactory product.

Very truly yours,

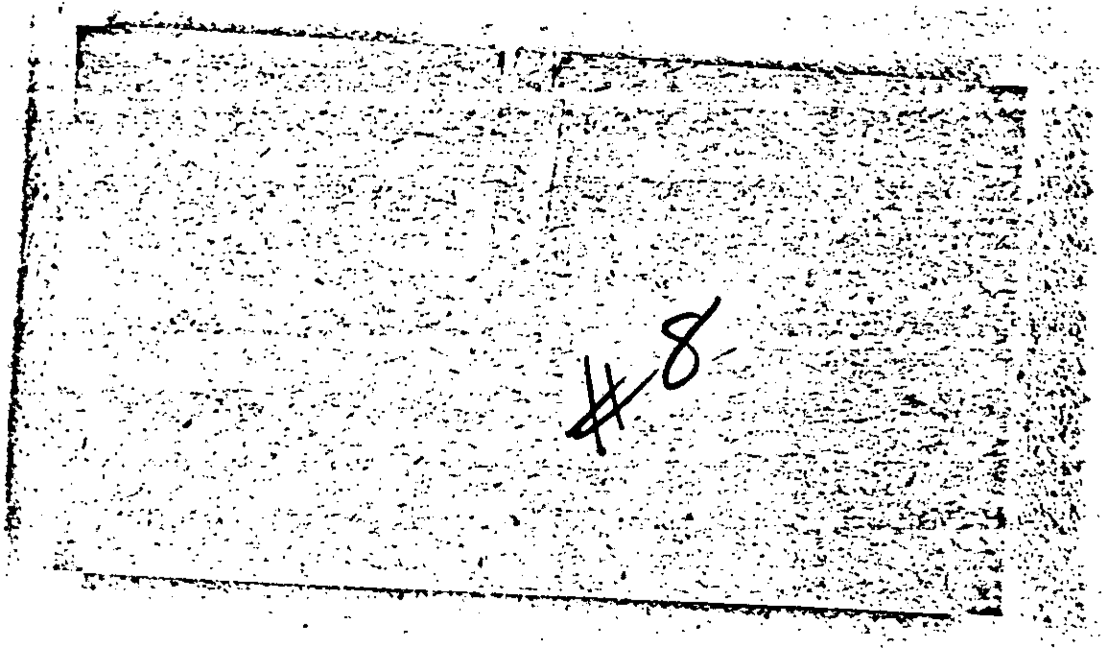
Julian P. Brodie

Julian P. Brodie

SIGNED AND AGREED TO THIS
19 DAY OF September 1946.

A Brothman

A. Brothman



#8

Analytical [illegible]

([illegible])

Iron   Ref. Welcher - Org. Reagents in Inorg. Analysis

p. 417 ff

I Thioglycolic Acid

amt Detectable: 0.001 mg Fe in a conc. of 1:10,000,000

amt Determinable .0025 to .025 mg Fe

Interfering Substances: As, Bi, cyanides, Co, Au, Pb, Mn, Hg^{+}, molybdates, Ni, Ag, Cu^{++}, sulfites, W, Uranyl, Zn

Reagent

a- add 4 cc of $HSCH_2COOH$ to 8 cc of NH_4OH in 50 cc of water

b. perchloric acid

c. H_2SO_4 - conc & 10%

d - HNO_3 - conc

e. NH_4OH - c.p. 28%

g - dissolve 1 gm pure Fe in dil H_2SO_4 add HNO_3, boil to expel oxides of N & HNO_3, & dil to 1 liter

Method

a. Heat 5 cc (sample) with 5 cc of H_2SO_4 and 0.5 cc 60% perchloric acid in a micro-Kjeldahl flask. Heat for 10 mins, cool, & repeat 0.5 cc addn of perchloric acid until color is colorless & free from excess perchloric acid.

b. Transfer to beaker & make alk to litmus by adding NH_4OH & then acid to litmus with conc. H_2SO_4, add an excess of 5 drops of conc. H_2SO_4

c. add 1 cc of thioglycolic acid reagent & 1 cc of conc NH_4OH & adjust vol to 25 cc. (violet-red color)

Cf. with standard.

---

p. 136 Willard

Further

c̄ forms

Ni - yellow

Co - yellow-red

cyanides - deep orange-yellow

Au - amber

[illegible] - Red

Pb - yellow to amber

Mn - amber

Hg^{++} - black

Mo - yellow-orange

Ni — reddish purple

W — blue (   )

Ag — amber

Sn^{++} — yellow

Uranyl — yellow

Dubsky & [illegible]   Mikrochimica Acta 2, 257 (1937)

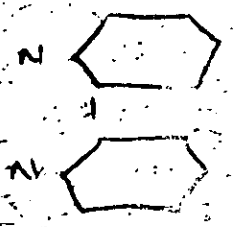
$Fe^{+++} \longrightarrow Fe(SCH_2COONH_4)_3$

violet red color

Fe^{++} does not give this reaction.

Fe^{++} Ref. Feigl Ed 2 p 97 "Spot Tests"

α-α' dipyridil



→ Soluble deep red complex

Fe^{+++} does not react.

Test useful where CNS^- test is no g.

Limit 0.03 γ Fe

Conc limit 1:1,666,000

Reagents: 2% soln of α-α'-dipyridil in dil HCl
or an alc. soln of the base.

Method — Treat a drop of the test soln with a drop of the reagent soln on a spot plate
→ red or pink color.

KCNS test for Fe

presence of phosphates, arsenates, oxalates, tartrates & other org. OH cpds, fluorides & many cpds which are stable complex Fe^{+++} salts can so reduce the conc of Fe^{+++} that the necessary ionic concn for reaction is never reached.

Hg^{+} & Hg^{++} also interfere

NO_2^{-} interferes

limit of ident. 0.25 γ Fe

Concn limit 1:200,000

Method - mix a dp. of the test soln with a drop of 1% KCNS soln. and a more or less deep red color appears.

Fe^{++}) Feigl p. 98

Dimethyl glyoxime

limit 0.04 γ Fe

Concn limit 1:125,000

Reagents 1% alc. Dimethyl glyoxime

Tartaric acid

NH_4OH

Fe^{++} forms soluble red inner complex in a [illegible] forms a [illegible]

Ni this interferes but if KCN is added the Ni salt dissolves & only the Fe++ salt remains.

To test for Fe++ in Fe+++, treat with tartrate → soluble complex stable in presence of NH_3.

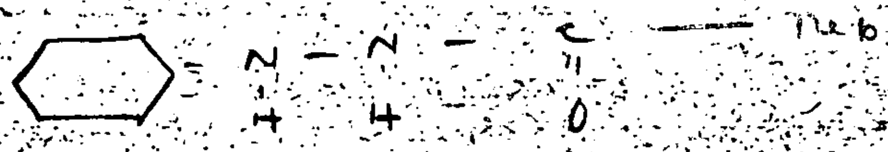
method - Reduce Fe+++ with 80% (H_2SO_3) or Hydroxylamine Hydrochloride.

mix a drop of the soln with a crystal of tartrate & then add a drop of alc. DMG followed by a little NH_4OH. according to the Fe++ content, a more or less intense red color appears which fades on standing due to oxidation of Fe++ complex.

Mellan p. 316

Cr

Reagent Diphenyl carbazide



amt detectable 0.00025 mg Cr in a conc of 1:200,000

amt determinable .005 to 0.05 mg Cr

Interfering substances Co, Cu, Mn & Ni

DPC soln. 1% in EtOH

Br water – (sat aq. soln)

Spot Test – Place a drop of the test soln on a plate & add 1 dr. sat Br-H2O. Then add 2N NaOH dropwise until the resulting soln is alk to litmus. Add a xtal of phenol & 1 dr of a 1% DPC soln & 2N H2SO4 dropwise until the red color of alk-DPC is discharged. If chromate are present, permanent violet-blue color develops

→

or

using 0.2 gms DPC diss in 10 cc AcOH (gl.) & dil to 100 cc with 95% EtOH

Qual. Procedure: To 5 cc of test soln add 1 cc of 6N NH4OH, acidify to AcOH, add 5 cc of DPC reagent & shake. If Cr is present → violet or violet red color. [illegible] with 3% H2O2

Amt detectable 0.001 mg Cr in 1:1,000,000
conc

Interfering constituents Ag & Zn.

Cr Benzidine Welcher p. 317

( ) Feigl p. 152

Mn & vanadates interfere

Benzidine soln — 0.1% in 7%, AcOH

Na_2O_2 soln — 20% (fresh)

Limit of identif. 0.25 γ

Dilution limit — 1:200,000

Method — place a drop of Na_2O_2 soln on a strip of filter paper, add a dr. of test soln & a dr. of benzidine soln. If $CrO_4^=$ is present, a blue [illegible] appears.

Mo phenylhydrazine

Limit detectable 0.006 mg in conc of 1:100,000

Method To 5 cc of test soln (contg alk molybdate) add 5 cc of PH soln (sat aq), 0.5 cc of HCl & heat → rise to blood-red color

or

mix 1 cc PH in 10 cc AcOH, place a drop of test soln on spot plate & add a dr. of PH reagent → red color.

detects 0.004 mg in conc of 1:160,000

Mo. <u>KCNS</u>

and detectable 0.001 mg in conc. of 1 : [illegible],000

Interfering substances Fe, Hg, [illegible]

<u>Dimethylglyoxime</u> Feigl p. [illegible]

<u>Ni</u> in presence of Fe^{+++}

limit of detection 0.5 γ Ni (in presence of 1000 times amount of Fe [illegible] soln)

limiting conc. 1 : 1,00,000

place on spot plate

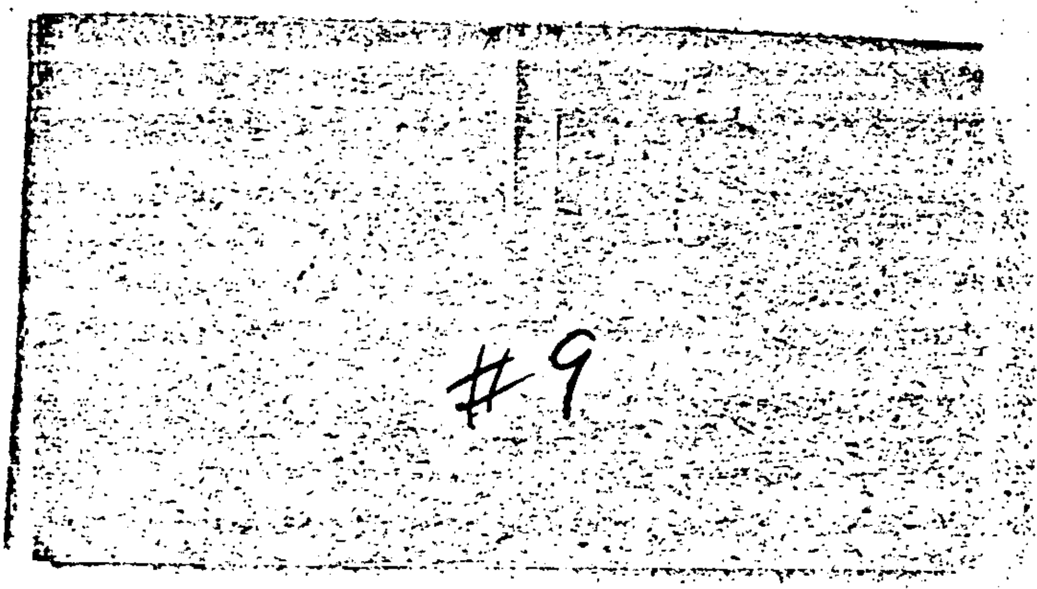
1 dp. test soln

1 dp sat. Na tartrate

2 dps sat. $NaHCO_3$

1 dp. alc. (0.1%) DMG

red Ni salt is formed at edge & surface of liq. due to lower S. T. of alc.



#9

PROGRAM OF WORK FOR THE CHINESE JOB

8/26/46 and tempus fugits

LAB SCHEDULE

1. Acetylene → Acetone	October 21, 1946
2. CO_2 and NH_3 → Urea	November 4, 1946
3. Electrothermic Processes a. Cyanamide b. Cyanide	December 1, 1946
4. HCN Generation	December 31, 1946
5. Acetylene Generation	December 31, 1946

OFFICE SCHEDULE

1. Preliminary Flowsheets	Already completed
2. Calculations	November 1, 1946
3. Instrumentation (preliminary)	August 30, 1946
4. Unit Process Equipment	November 30, 1946
5. Specified Equipment	March 30, 1947
6. Piping, etc.	February 28, 1947
7. Power Distribution	February 28, 1947
8. Steam and Water Distribution	February 28, 1947
9. Building Design	March 30, 1947
10. Power Plant	December 31, 1946
11. Layout and Placement Drawings	April 30, 1947
12. Lab. Facilities	December 31, 1946

#10

[illegible]

Fe as ion

α-α'-dipyridyl { limit 0.03γ Fe
conc. limit 1:1,666,000

2% in alc.

method - treat dp on spot plate → red or pink circle

Cr as $CrO_4^=$

Diphenylcarbazide { limit 0.001 mg Cr
conc. limit 1:1,000,000,000

diss 1 gm in 50 cc. AcOH
& dil to 500 cc with 95% MeOH

method - to 10 cc of test soln. add 2 cc of 6N NH_4Cl (1) acidify to AcOH), add 2 cc of DPC reagent & shake. If Cr is present → violet or violet red color.
(2) acidify with 3% HCl

Mo as molybdate

phenylhydrazine { limit 0.0004 mg
conc. limit 1:160,000

diss 10 cc of phenylhydrazine in 50 cc AcOH

method - place a drop on a spot plate & add a drop of ph. reagent → red color

Ni in presence of Fe

Dimethylglyoxime [illegible]
limit 0.0[illegible]1 mg
conc. limit 1: 500,000

0.1% in alc

method –
1 drop test soln.
1 drop sat. Na tartrate
2 drops sat Na[illegible]
1 drop alc DMG

→ Red Ni spot at edge & surface due to lower S.T. of alc.

No. 1

0.5 mg. diff. = 2.6 [illegible]

12.2112 am. orig

No. 2

11.3038 am. orig
11.3033
0.0005

11.3029 [illegible]
11.3021 [illegible]

Cu – 10 cc → < 0.001 mg Cu (1:1,000,000,000) – [illegible] 0.0033 mg
Fe – 1 cc → 0.00066 ~~mg~~ Fe (1:1,660,000) [illegible] 0.0048 mg
Na – color yellow tinge

ClCH₂ – 20 NaOH
ClCH₂COOH
ClCH₂
H₂O

No. 3

10.[illegible] am. orig
10.[illegible]
0.000[illegible]

10.7742 12 M – 4/16
10.7740 11 AM 4/17
0.0002

No. 4

7.4103 am. orig
7.4097
0.0006

7.4092 [illegible] 4/16
0.0005 lost
7.4088 11 AM 4/17
0.0004

HCl
ClCH₂COOH
NaNO₃
ClCH₂COOH
NaOH
NaCl
H₂O

#11

Prep. of borate of α-OH i-B acid
( )

[illegible]

1 mole + 2 moles H_3BO_3
400 cc toluene

HOH taken off = 39 cc ≈ 17 g, two of
$H_2B_4O_7$

$4H_3BO_3 \longrightarrow H_2B_4O_7 + 5HOH$
4 × 61.8 157.3

$\frac{157.3}{\cancel{4 \times 61.8}\ 2} \times \cancel{4 \times 61.8} = 78.7$ gms $H_2B_4O_7$

$6H + \boxed{2B_4O_7 \cdot HOH} \longrightarrow 2B< + 2H_3BO_3 + HOH$
1 mole combines with 5 of α-OH acid

78.7 × 0.97 = 68.5 gms actual $H_2B_4O_7$

Using only 75% of the

68.5 × 0.75 = 51 gms

$H_3C - \overset{OH}{C} - CH_3$ $\quad C^{O}_{OH}$ Mass = 4C 48, 8H 8, 3O 48, 104

$\frac{104.5}{157.3} \times 51 =$ [illegible] gms α-OH acid [illegible] of [illegible] of [illegible] O. H. D. Baird

( )

[illegible] 8.1.7.4 [illegible] a a 25.9 [illegible]

6.9 [illegible] 0.30 = [illegible] 9 [illegible].

Dehydration of AcOH via H_3BO_3 - Toluene
( )

<u>Charge</u>

186 gms. Toluene = 2 mols

60 gms. AcOH = 1 mol

93 gms. H_3BO_3 = 1.5 mols

plus 23 gms. added Toluene for Trap)

Distilled thru column to Bidwell-Sterling Trap

Time	Pot °C	Lower Layer cc	Notes
7:15 PM	—	0	
8:00	114	13	
8:30	103	[illegible]	
9:00	114	5 ✓	

Titration $\frac{40}{5}$ × 186 × 0.1054 × 0.060 = 23.8 gms.
out of 40

Final titration $\frac{[illegible]}{5}$ × 177 × 0.3054 × 0.060 = 45 gms.
AcOH

69
$\frac{45}{24}$ gms. HOH

$H_2B_4O_7$

$B_2O_3 \cdot H_2O$

$\frac{54}{123.6}$ × 93.2 = 42 gms

H_3BO_3 → $B_2O_3 \cdot H_2O$ + 2 H_2O
123.6 36

$\left(\frac{5}{6} \times 3 = \frac{5}{2} = 2\frac{1}{2}\right)$

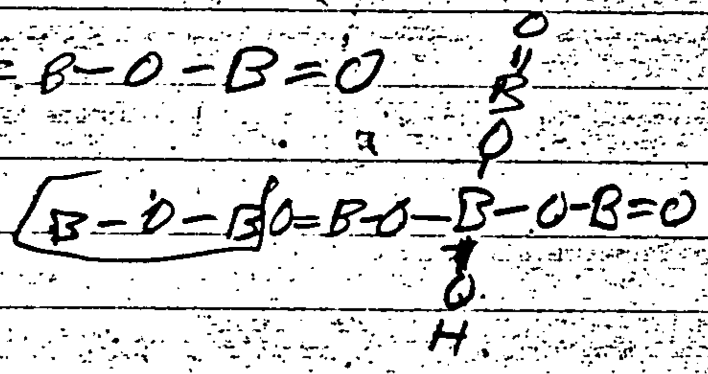
$2H_3BO_3 \longrightarrow B_2O_3 + 3H_2O$

$4H_3BO_3 \longrightarrow H_2B_4O_7 + \underbrace{5H_2O}$

12

$HO=B-O-B-O-B-O-B-OH$

$O=B-O-B=O$



$$\boxed{B-O-B}O=B-O-\underset{\substack{| \\ O \\ H}}{\overset{\substack{O \\ \| \\ B \\ | \\ O \\ |}}{B}}-O-B=O$$

Hydrolysis of acetone cyanohydrin

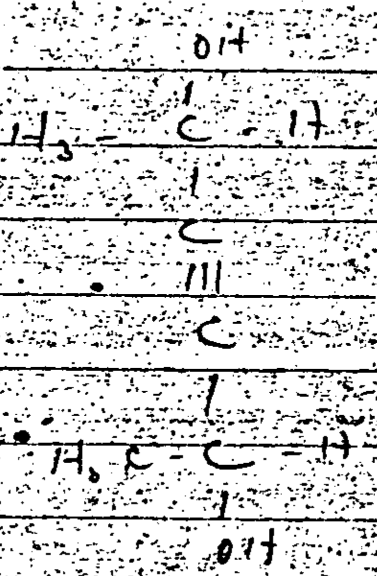
( )

1000 cc = 932 gms.

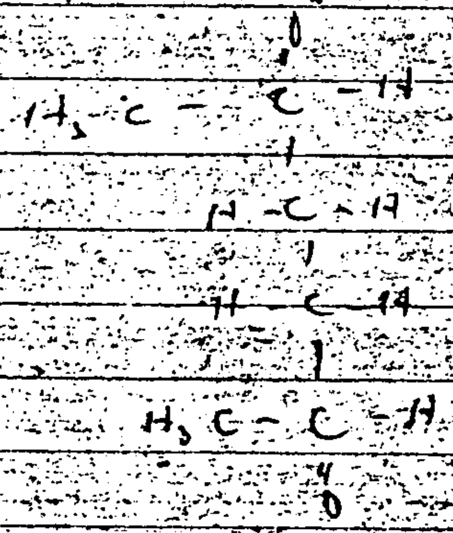
$932 \times \frac{1.32}{1.00} \times \frac{1}{1.18} = 1040$ cc conc HCl

Start adding HCl $10\frac{30}{AM}$.

Finish adding HCl Noon.



OH
H3 – C – H
C
C
H3 C – C – H
OH



O
H3 C – C – H
H – C – H
H – C – H
H3 C – C – H
O

Diol = 142 M. 14.2g → B. [illegible] 3.6 cc

12.37

H_3BO_3 = 61.84 $\frac{0.2M}{3} = \frac{12.4}{3}$ = 4.13g

10% x 3 = 4.55

14.2g diol = 0.1M

5.50g H_3BO_3 =

40 cc. C_6H_6

Pot 83

	Pot	Column	HD
1.45	83°	70°	0
6.45	100°	77°	2.6

#12

Cell characteristics 1N H_2SO_4 (a) Decinite anode (120cc sol's outside por. cup)

E	I
3,3	.195
3,47	.232
3.68	.281
4.01	.493
4.52	.861

Cell characteristics 1N H_2SO_4 + 1.42g. diol

E	I	E	I
3.0	.215 (.195	3.51	.222
3.32	.212	3.51 volts 6/12	
3.4	.226	11:30 – .261 Amp	
3.46	.242	12:00 ~~Reduced to 3.48 + 2.50~~	
3.57	.273	At 12:00 reduced to 3.33 + .18	
3.89	.445	at 8	(3.50) a 0.170
3.71	.400		3.217
3.66	.363	3.28	.181
.363	.352	3.38	.208
.361	.335	3.45	.221
.360	.323	3.55	.296
.358	.311	3.80	.260
3.57	.300	Recovered 1.28 g.	
3.55	.290		
3.52	.28		

22)1[illegible]0.000
88
170

22

Ni beaker - $\pi d = 3.14 \times 7$ = 21.98 cm Depth of 4.55 cm = 1 Decimeter
πr^2 = 38.5 sq cm 38.5 x 4.55 = 175 cc, (165

Cell cont'g. 165 cc 2N NaOH outside cup

Voltage of cell after # Ni ca. 0.3 volt - kept falling

E	I
2.30	.105
2.38	.153
2.51	.236
2.62	.325
2.78	.427
2.95	.595
3.19	.840
3.35	1.05

Added 4.26 dist

E	I
2.34	.108
2.44	.152
2.59	.233
2.70	.311
2.79	.379

6H $\frac{1.61}{9.66}$ amp hrs, 84 84 $\frac{.06}{46(8}$

841 $\frac{.06}{5000}$ 504

75cc. 1N H_2SO_4 + 5g [illegible] outside porous cup.

35 - 1st reboiling

E	I		E	I
3,12	,202		2,99	,087
3,06	,165		3,05	,120 ✓
3,16	,203		3,20	,134
3,20	,220		3,33	,190
3,23	,233		3,29	,175
3,38	,2405		3,26	,160
3,32	,252		3,22	,158
3,39	,262		3,19	,140
3,44	,277		3,16	,123
3,50	,304		3,12	,111 ✓
,59	,335		3,38	,197
3,64	,360		3,40	,203
3,75	,407		3,50	,236 ✓
3,83	,448		3,44	,219
,95	,499 4:15		3,45	,220
,93	,087		4,24	,592
07	,120	4,5		
50	,173	1,85		
,20	,175	6,35		

$HC\equiv COH \rightarrow CH_2=C=O$

Sunday. 2/29/48

Stirred 21.3 g. glycol with 112 cc. conc HCl 2 hrs.
a Dil'd w/ ether
Sep'd & washed.

	b.p.	$n_D^{21.5}$	n_D^{23}
1.	68-72/18mm	1.4285	1.4778
2	72-76/15mm.	1.4880	6.8g.
3	76-8/15mm.	1.4939 (21)	6.6g.

126.59
25.25
151.84

164.05 ✓
151.84
12.21

12×35
60
36
420
35
455

432
420

18×24
72
36
432

420

1

12.87
20.08
5.44
38.39

123.36
25.25
148.61

164.05
148.61
15.44

15.44×35
75
45
525
15
540

#13

1)116.5 $\frac{22}{114}$

$ClCH_2COONa$ sol'n

$ClCH_2COONa$	1690 lb
$ClCH_2COOH$	150 lb
H_2O	4253
CO_2	8.26

H_2S	67.4	$HSCH_2COOH$	233
$ClCH_2COONa$	3.13	Na_2SO_4	228
$NaHS$	27.3	$NaCl$	153
$HSCH_2COONa$	302	H_2SO_4	5.3
$NaCl$	153.7	H_2O	1729

H_2S	62.4
$ClCH_2COONa$	31.7
$NaHS$	41
$HSCH_2COONa$	274
$NaCl$	139.5
H_2O	1612

~~2.1 N thioglycol acid = 198.5 g/liter~~ $\frac{1}{2.65}$ .89

~~H_2S 16.85~~

~~$ClCH_2COONa$ 7.98 — 5.83 $ClCH_2COOH$ + 3.27 g. Na_2CO_3~~

~~SCH_2COONa 68.5 — 55.3 g $HSCH_2COOH$ (27 cc.) + 25.4 g. NaOH~~ 28

~~NaHS 10.3 — 7.70 g NaOH~~ 2.8 12 $\frac{3}{4}$ 1

~~NaCl 34.88~~

~~H_2O 403~~

1 NaHS 3

③

$\frac{102}{193.5}$ 28 g.

✓ $HSCH_2COOH$	56	~~38~~
✓ Na_2SO_4	56	~~28~~
✓ NaCl	38	19
✓ H_2SO_4	1.3	0.65
H_2O	432	218
✓ 1L Sol		

~~Extract 530 cc. once with equal vol. butyl ether~~

$ClCH_2COONa$	[redacted]
$ClCH_2COOH$	15
H_2O	425.3

$\left\{\begin{matrix}13.8g\\15g\end{matrix}\right\}$ = 153 g. $ClCH_2COOH$ + 77.5 g. Na_2CO_3

30°

— 76.5 g. $ClCH_2COOH$ + 38.8 g Na_2CO_3

202.7 cc. H_2O

15°C

✓ H_2S	8.43
$ClCH_2COOH$	2.92
Na_2CO_3	1.64
$HSCH_2COOH$	27.7
NaOH	12.7
NaOH for NaHS	3.87
NaCl	17.44
H_2O	201.5 cc.

Extract 530 cc. once with equal vol. butyl ether